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Theoretical Study of Diffusion of Ga Atoms on a H-Terminated Si Surface

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Recently we have found that scanning tunneling microscope (STM) images of bar structures are obtained when Ga atoms on an H-terminated Si(100) surface are observed at 100 K. We reveal that the STM images correspond to a one-dimensional thermal diffusion of single Ga atom which is terminated by dihydrides. In order to verify this, we performed first-principles calculations for the electronic states of this system. As a result, we found that the calculated stable position of a Ga atom and the direction of the diffusion agree with experimental results. The energy barrier for the diffusion of a Ga atom is found to be 0.2 eV, which is a reasonable value for explaining the experimental results. Moreover, the calculated temperature range, where the one-dimensional diffusion takes place, agrees with experimental results. From these results, we conclude that the bar is an image of one Ga atom, directly reflecting the spatial probability distribution of Ga atomic motion.

Microscopic studies of solid surfaces have been very important due to the recent remarkable progress in fabrication technology of nanometer-scale structures on solid surfaces. In particular, an atomic-scale-fabrication technique that uses a scanning tunneling microscope (STM) has created new possibilities for developing nano-scale electric devices.[1, 2, 3, 4, 5] In order to produce and evaluate such small structures, we need to know more precisely how the atoms on the solid surface behave and what kind of environment the surface provides. It is also important to understand the motion of the atoms on surfaces since diffusion is one of the essential parameters controlling crystal growth.[6, 7]

Recently Hitosugi *et al.*[8] have found that STM images of the bar structure (which we call Ga-bar) are obtained when Ga atoms on a hydrogen-terminated silicon (100)2×1 surface are observed at 100 K. A Ga-bar has a linear shape and lies between the two Si-dimer-rows as shown in Fig. 1. The lengths of these structures range from 2 to 10 nm. The height of Ga-bar depends on its length, i.e., a long Ga-bar has a lower height than a short Ga-bar. In some cases, the STM images of intermittent Ga-bar are obtained where some parts of the bar vanish abruptly, indicating the absence of the Ga atom under the tip at that moment. These two experimental facts suggest that the Ga-bar is not a row of Ga atoms, but actually one Ga atom moving one-dimensionally, and this raises some important questions: (1) Why is the Ga-bar image obtained only in the narrow temperature range near 100 K? (2) What terminates the bar? (3) How many Ga atoms are moving in one Ga-bar?

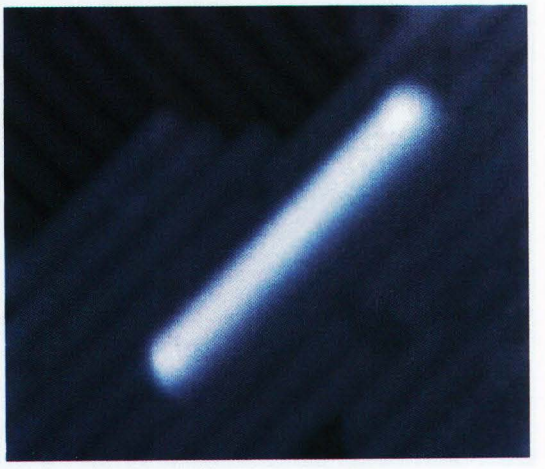

Figure 1: A 12×10 nm STM image of Ga-bar on an H-terminated Si(100) surface after ref. [8]. ($V_s = -2$eV, $I_t = 20$pA).

We addressed these questions by performing first-principles calculations for this system and here we discuss them from a theoretical view point. Throughout this paper, calculations are performed within local-density-approximation (LDA) using plane-wave-based ultrasoft pseudopotentials[9, 10]. The energy cutoff is taken as 9 Rydberg (Ry). The criterion of the convergence of the geometry optimization is that all of the forces acting on each atom

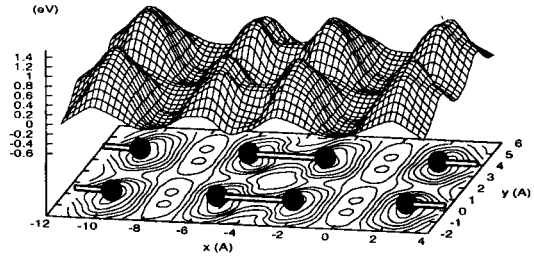

Figure 2: A potential surface for a Ga atom on an H-terminated Si(100) surface. The positions of peaks correspond to the positions of the H atoms.

are within 1×10^{-3} Hartree/a.u. Two kinds of unit cells (4×2 and 4×4) with five silicon layers are used for the calculations.

First we calculated the potential surface for the Ga atom on the hydrogen-terminated silicon surface. For that purpose, we put the Ga atom on appropriate grid points and calculated the electronic structures of the system. For each position of a Ga atom, the total energy of the system is calculated by optimizing the positions of the other atoms and the vertical position of the Ga atom. The obtained potential surface is shown in Fig. 2. From this figure, it can be seen that the most stable position of a Ga atom lies between the two Si-dimer-rows and that the energy barrier is the lowest when the Ga atom moves along the Si-dimer-rows. This result well explains the STM image of Fig. 1. The hopping rate of the Ga atom from one stable position to another can be expressed as

$$\Gamma = \nu \exp\left(-\frac{\Delta E}{k_B T}\right), \qquad (1)$$

where ΔE is the activation energy and ν is the frequency of the oscillation of the Ga atom at the stable position. According to our calculated result, these values are estimated as $\Delta E_{\|} = 0.215$(eV) and $\nu = 1.56 \times 10^{13}(\mathrm{s}^{-1})$. The energy barrier in the direction perpendicular to the Si-dimer rows is also calculated and the value is $\Delta E_{\perp} = 0.469$(eV). Using these values, the hopping rate Γ is shown in Fig. 3 as a function of the temperature. Because the scanning time of one STM image is about 20 seconds, the critical hopping rate above which the images of moving atoms can be obtained is roughly estimated as $100(\mathrm{s}^{-1})$. Figure 3 shows that a Ga atom can hop to the direction parallel to the Si-dimer rows at a temperature above 100 K. This figure also shows that a Ga atom can hop toward the direction perpendicular to the Si-dimer rows at a temperature above 200 K so that a Ga atom can diffuse two-dimensionally. Therefore, the Ga-bar images can be obtained only in the temperature range between 100 - 200 K. This calculated result well explains the question of why the image of the Ga-bar is obtained only in the narrow temperature range near 100 K.

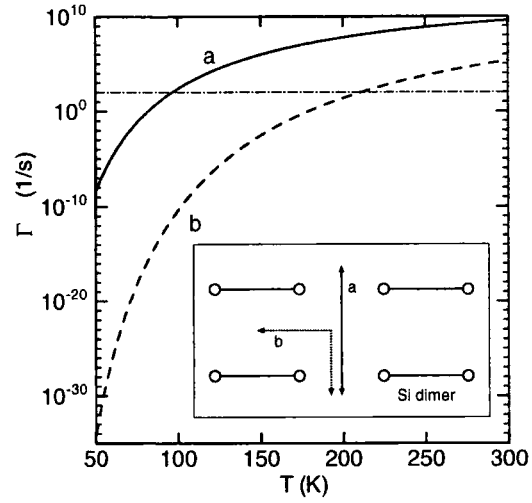

Figure 3: (a) Solid line shows the hopping rate (Γ) of the Ga atom along the Si-dimer rows. (b) Dashed line shows the hopping rate in the direction perpendicular to the Si-diner rows. The horizontal dashed-dotted line at $\Gamma = 100$ indicates a rough estimation of the critical hopping rate above which the STM image of moving atoms can be obtained. The inset shows the direction of the diffusion.

Next we will discuss what terminates the Ga-bar. From the STM images, it seems that the dihydride structure where two hydrogen atoms are bonded to the Si atom terminates the Ga-bar. If this is true, the potential barrier for a Ga atom at the dihydride should be larger than that at the normal structure (monohydride) where a single hydrogen atom is bonded to the Si atom. In order to check this point, we calculated the potential barrier for a Ga atom at the dihydride along the direction parallel to the Si-dimer rows, in the same manner as the calculation for the potential surface. The obtained result is shown in Fig. 4. It can be seen from this figure that the Ga atom in the channel between the two Si-dimer rows encounters the large potential barrier at the dihydride and the Ga atom can not go beyond the dihydride.

Furthermore, we calculated the STM image of the dihydride and compared it with the experiment. Experimentally, there are two separate blight spots and a hole between them at the position of dihydride when the sample bias is negative, and there is one blight spot at the center of the position of the dihydride when the sample bias is positive as shown in Figs. 5(a) and (b). The calculated result shown in Figs. 5(c) and (d) well agrees with the experimental one. Due to the good agreement of these two theoretical results with the experiments, we can suppose that the dihydride terminates the Ga-bar.

Next we investigated the possibility of having two

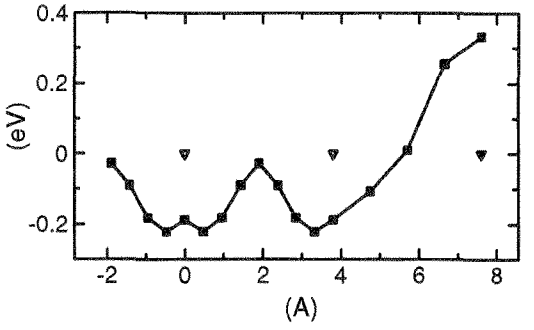

Figure 4: The potential surface for a Ga atom between the two Si-dimer rows. The positions of Si-dimers with monohydride and with dihydride are marked by open and closed triangles.

or more Ga atoms in one Ga-bar (in one channel). For the case where two Ga atoms are adsorbed on the surface, we obtained several metastable structures by first-principles calculation and found that both of the Ga atoms lie in the channel between the two Si-dimer rows and are bound to each other in the most stable structure as shown in Fig. 6(a). In the next stable structure, both of the Ga atoms also lie in the channel and are bound to each other as shown in Fig. 6(b) and the total energy is 0.064 eV higher than that of the most stable structure. If we assume that the two Ga atoms in one channel move together keeping bonded each other, they will take the structures of Fig. 6(a) and (b) alternately. When the structure changes from one to the other, one Ga atoms should go beyond the potential barrier while the other should not. The height of the barrier can be expected to be approximately the same as the case of one Ga atom in one channel. On the other hand, if we assume that the Ga atoms move separately, 0.825 eV is required to separate the two Ga atoms while the height of the energy barrier will be not lowered by the separation. Therefore, we consider that the two Ga atoms move together keeping bonded each other, if there are two Ga atoms in one Ga-bar. This means that the Ga-bar image is obtained not only when a single Ga atom is adsorbed, but also when the two Ga atoms are adsorbed in the same channel terminated both ends by dihydrides.

The temperature dependence of the diffusion of the multi-atom Ga-bar may be different from that of a single atom. Detailed calculation of the potential surface for two or more Ga atoms is required to discuss that point theoretically and the calculation is in progress. Experimentally, a higher resolution STM image can distinguish between the single atom Ga-bar and multi-atom Ga-bar, according to the spatial difference of the potential surfaces in two cases.

Finally, we should mention that the spatial variation of the potential surface for the Ga atom can be seen as the change of the height of the Ga-bar image. For example, the calculated potential energy at the stable site adjacent to the dihydride is 4 meV lower than that of the other stable sites. Provided that the tip-sample interaction is negligible, this energy difference gives the ratio of visiting probability, (adjacent site)/(other site)= $\exp(-4\mathrm{meV}/kT) = 1.59$ at 100 K. From this, we can estimate how the height difference results by using the fact that the tunneling current I at one stable site is proportional to the visiting probability of the Ga atom and $I \propto \exp[-(2\sqrt{2m_e}/\hbar)\sqrt{\phi}d]$[11]

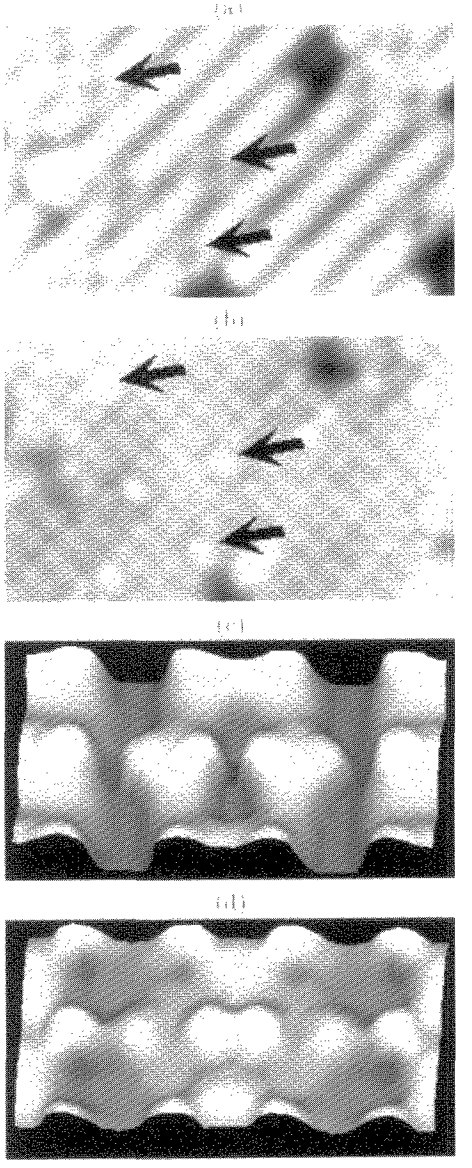

Figure 5: Experimental STM images of dihydrides with (a) $V_s = -2.0$V and (b) $V_s = +2.0$V, and calculated STM images with (c) $V_s = -2.0$V and (d) $V_s = +2.0$V.

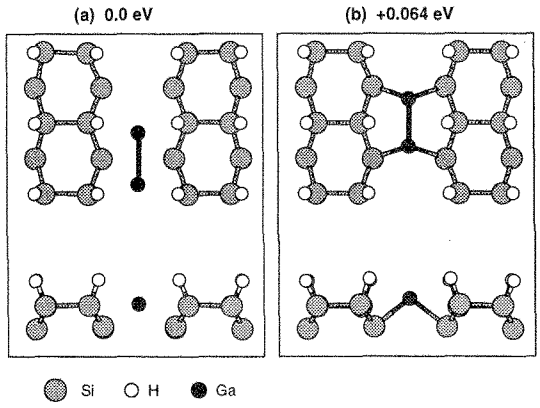

Figure 6: (a) The most stable structure and (b) the next stable structure when two Ga atoms are adsorbed.

where m_e and d are the electron mass and the tip-sample spacing. The work function ϕ is estimated to be 5.55 eV from our additional calculation. According to these relationships, the height difference of Ga-bar image between the adjacent site and the other sites is estimated as 0.018 nm. Actually, the STM image of Ga-bar (see Fig. 1) has small protrusions at the both ends and the height of these are 0.02 ± 0.003 nm. Thus, our theoretical calculation is in excellent agreement with the experiment. We expect that the Ga-bar image can be used for the purpose of investigating the surface potential. The small difference in the surface potential can be viewed as the relative height difference of the Ga-bar images.

In conclusion, we have confirmed that the Ga-bar is the STM image of one Ga atom or a few Ga atoms moving in the channel between the two Si-dimer rows whose ends are terminated by dihydride structures. The Ga-bar image has the potential to be used as a technique for viewing the subtle changes of the surface and surface potentials.

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