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The influence of strain on the diffusion of Si dimers on Si(001)

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Abstract

The influence of lattice mismatch-induced *tensile* strain on the diffusion of Si dimers on Si(001) has been studied. The rate of surface diffusion of a Si dimer *along* the substrate dimer rows is relatively insensitive to *tensile* strain, whereas the rate of diffusion for a Si dimer *across* the substrate dimer rows is significantly enhanced. The insensitivity of the *along* row diffusion rate for *tensile* strain is attributed to the presence of a dissociative intermediate state of the ad-dimer during diffusion rather than diffusion as a solid unit. © 2000 Published by Elsevier Science B.V. All rights reserved.

Keywords: Scanning tunneling microscopy; Silicon; Surface diffusion

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During growth of heteroepitaxial thin films it is well established that lattice mismatch-induced strain plays an important role. The thermodynamically determined surface morphology has been investigated for many heteroepitaxial systems. For example, the Ge on Si(001) system has led to a wealth of interesting observations. Among them are the formation of $2 \times n$ reconstruction [1], reversal of step-edge roughness [2], submonolayer Ge–Si interface mixing [3], and transition to three-dimensional growth [4,5]. In most cases, however, thin films are grown far from thermal equilibrium. The morphology is governed by kinetics rather than by thermodynamics. The influence of strain on kinetics then becomes a key factor in determining surface morphology and reconstruction.

The influence of strain on surface diffusion has been a topic in several studies of metal systems. Experimentally, Brune et al. [6] have studied isotropic diffusion of Ag atoms on strained Ag(111). The diffusion barrier decreases significantly for a 4.2% *compressive* strain of the Ag(111) surface. Calculations on this metal system performed by Ratsch et al. [7] are in good agreement with these experiments. Ratsch et al. have found that in the range of ±5% strain the theoretically determined diffusion barriers exhibit a linear dependence on strain (*tensile*, respectively *compressive*, strain resulting in an increase, respectively decrease, of diffusion barriers). Finally, Schroeder and Wolf [8] have studied the effect of strain on the diffusion barrier of (001) surfaces. They have considered three different crystal structures: simple cubic, bcc and fcc. In all three cases the adatom diffusion barriers increase for a *tensile* and decrease for a *compressive* strain. For strains up to ±5% the height of the activation barrier for surface diffusion varies linearly with strain.

The influence of strain on adatom diffusion has been studied theoretically for the homoepitaxial Si(001) system. Roland and Gilmer [9] have performed a molecular dynamics simulation for Si adatoms diffusing on Si(001). They have used a Stillinger–Weber potential in order to address the

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influence of strain. In their study they have found that for 3% *compressive* as well as for 2% *tensile* strain the diffusion barrier *along* the dimer rows is lowered by approximately 10%. Spjut and Faux [10] have also found a decrease of the diffusion barrier. A *tensile* strain of 1% lowers the adatom diffusion barrier *along* the dimer rows by approximately 9%. In contrast to the plain trend for metal systems, no clear trend has been found for the influence of strain on the adatom diffusion rate on semiconductor surfaces.

For semiconductor Group IV (001) surfaces, the influence of strain on surface diffusion is additionally complicated. Firstly, the building blocks for island and layer formation are not the adatoms, but a cluster of two adatoms, the so-called ad-dimer. Experimental studies have shown that these ad-dimers are formed either on top of or in the trough between the substrate dimer rows at temperatures below and near room temperature [11–14]. Secondly, surface reconstruction is responsible for anisotropic surface diffusion. Ad-dimers have a preferential diffusion direction *along* the substrate dimer rows [12–14]. A slower diffusion pathway of Si dimers *across* the substrate dimer rows has also been observed on both Si(001) [15] and Ge(001) [16]. The anisotropy in these rates for Si dimers on Si(001) has been found to be about 5×10^3 at 450 K [15] and about 10^3 for Si dimers on Ge(001) at room temperature [17]. Theoretically, dimer formation and diffusion have been studied for the Si on Si(001) system [18–23]. The influence of strain on the diffusion of dimers has not, however, been addressed theoretically.

The experiments have been performed in an ultrahigh vacuum (UHV) chamber with a base pressure of 10^{-10} Torr. The UHV chamber contains the scanning tunneling microscope (STM) and a silicon evaporator. Nominally flat clean Ge(001) surfaces have been prepared by cycles of sputtering with Ar^+ ions and annealing at 1100 K. To evaporate silicon atoms onto the clean substrate a nearby silicon crystal is heated to about 1450 K, resulting in a deposition rate of about 0.4 ML/min. In the first sequence of experiments about 0.01 ML of Si has been deposited on a nearly defect free Ge(001) surface at room temperature. In the next sequence of experiments strained Si surfaces have been used as an initial surface. Strained Si surfaces have been prepared by depositing about 1 ML of Si (0.4 ML/min) on a Ge(001) sample at 525 K. A growth temperature of 525 K is sufficiently low to avoid intermixing of the Si/Ge interface. The growth conditions allow the development of monolayer high Si islands with areas of typically 1000 nm^2. The pseudomorphic Si overlayer is under *tensile* strain in order to accommodate the 4.2% difference in lattice spacing. After radiation quenching to room temperature the surface is imaged with STM. An example of such an island is shown in Fig. 1. In the third sequence of experiments a bare Si(001) surface has been used. A clean Si(001) surface is obtained by resistively heating up to about 1400 K. In the final step 0.01 ML of Si is deposited at room temperature. After the final deposition, sequential images ('movies') have been recorded of the diffusing species on all three surfaces in a temperature range of 300–350 K. Special attention has been paid to the establishment of the temperature. For temperatures above room temperature the entire vacuum system has been externally heated until the temperature was stabilized. The external temperature of the equilibrated vacuum system has been measured accurately with a thermometer.

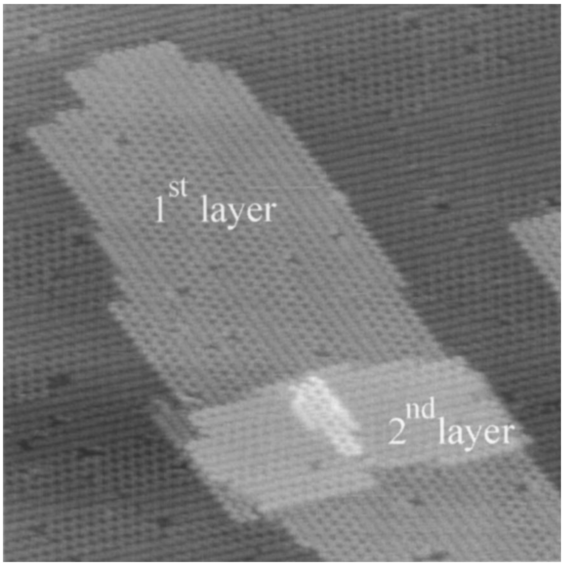

Fig. 1. Strained Si(001) surface; large Si island on a Ge(001) substrate, image size 40×40 nm^2; sample bias -1.6 V, current 0.4 nA.

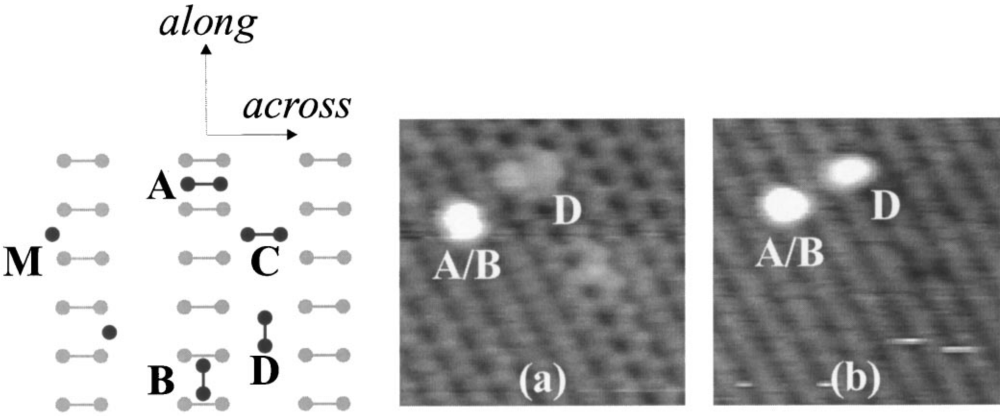

Fig. 2. Schematic monomer and dimer positions (black) on reconstructed (001) surface (gray). Filled state (a) and empty state (b) image of an on-top Si dimer (A/B) and a Si dimer in a trough position (D) residing on a Ge(001) surface; sample bias ±1.6 V, current 0.5 nA.

In STM images both on-top as well as in-trough Si dimers have been found. The ad-dimer is positioned between two surface dimers. In Fig. 2 Si dimers on a Ge(001) surface are shown next to a schematic drawing of the ad-dimer configurations on a reconstructed (001) surface. The on-top dimer (labeled A/B) is visible in both filled and empty state STM images, whereas the trough dimer (labeled D) is visible in the empty state image but quite faint in the filled state image. The C configuration is only observed in clusters of C dimers [16] for Si on Ge(001), but has a similar appearance as the D configuration. The discrimination between on-top and in-trough dimers holds as well for Si dimers on strained as on bare Si(001).

Firstly, the focus will be on the dimers located on top of and moving *along* the surface dimer rows. A single ad-dimer moving over the surface can be incorporated in larger clusters or step edges. This loss of single ad-dimers makes observation of diffusion difficult. In some cases, however, an on-top dimer is trapped between a pair of distant defects that confines its motion to a limited area of the surface. This makes the diffusion of the ad-dimer accessible for prolonged observation. In a recent report [17] we studied the diffusion of Si dimers on bare Ge(001). At room temperature the on-top Si dimers perform a one-dimensional random walk *along* the substrate dimer rows and have a surface diffusion rate of 0.10 ± 0.01 Hz.

For Si dimers on strained Si(001) diffusion *along* the surface dimer rows is also observed at room temperature. Three frames from a movie of an on-top Si dimer on a monolayer high Si island are shown in Fig. 3. In the upper right corner of the images a second layer Si island serves as reference. The marker is situated at the Si dimer position of the first image (Fig. 3a). The Si dimer diffuses one position towards the island (Fig. 3b) and returns to its original position after 450 s (Fig. 3c). From more movies like this, a diffusion rate of $(1.4 \pm 0.35) \times 10^{-3}$ Hz has been obtained at room temperature. It should be noted that we have taken into account only those dimers that are not attached to (or in close proximity to) surface defects. Recent STM studies [13,24] have revealed that surface diffusion can change locally due to these defects. The reported *along* row diffusion rates for Si dimers on bare Si(001) at room temperature are $(1.1 \pm 0.35) \times 10^{-3}$ Hz and $(0.44 + 0.31/-0.25) \times 10^{-3}$ Hz by Swartzentruber [13] and Krueger et al. [14], respectively, both using a tracking tunneling microscope (TTM). These rates are comparable with the diffusion rate for Si dimers on strained Si(001).

In order to investigate this similarity, Arrhenius plots of the *along* row diffusion rate are shown in Fig. 4. The measured rates[1] for Si on strained

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[1] The measured values and error bars have been calculated from statistical analysis [25,26] and by assuming random walk behavior.

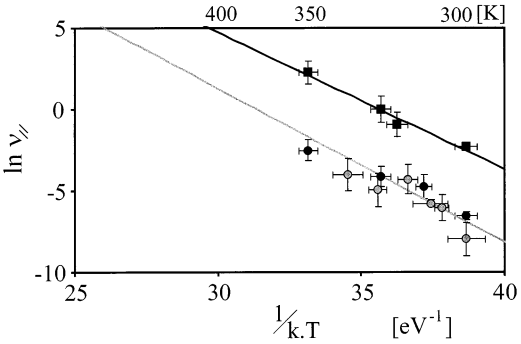

Fig. 4. *Along* row diffusion rates of a Si dimer on strained Si(001) (black circles), on bare Si(001) (gray circles) and on Ge(001) (black squares).

Si(001) and bare Ge(001) are compared with results for Si on bare Si(001). The diffusion rates of Si on Ge(001) are well above the rates of both Si on strained and bare Si(001). A linear fit of the Si on Ge(001) rates yields a diffusion barrier of 0.84 ± 0.09 eV and an attempt frequency of $10^{13.0 \pm 1.4}$ Hz (black line). The *along* row diffusion rates for Si on strained Si(001) are close to the rates of Si on bare Si(001). The gray line (0.94 eV, $10^{12.8}$ Hz [13]) is used as a guide. Interestingly, the influence of strain on the *along* row diffusion rates turns out to be small in the temperature range measured.

The *along* row diffusion rate of Si on Si(001) has been studied intensively. In Fig. 5 the diffusion rates obtained by Dijkkamp et al. [12], Swartzentruber [13] and Krueger et al. [14] are compared with the rates obtained in this work. In the temperature range measured the diffusion rates are in reasonable agreement with the existing data. Significant tip-induced movement of the ad-dimer near room temperature, as suggested by Krueger et al. [14], is absent since diffusion rates of TTM and standard STM overlap. Note: with standard STM the time spent above an ad-dimer is a small fraction (about 10^{-4}!) of the total scan time, whereas in TTM the tip is permanently in close proximity to the ad-dimer.

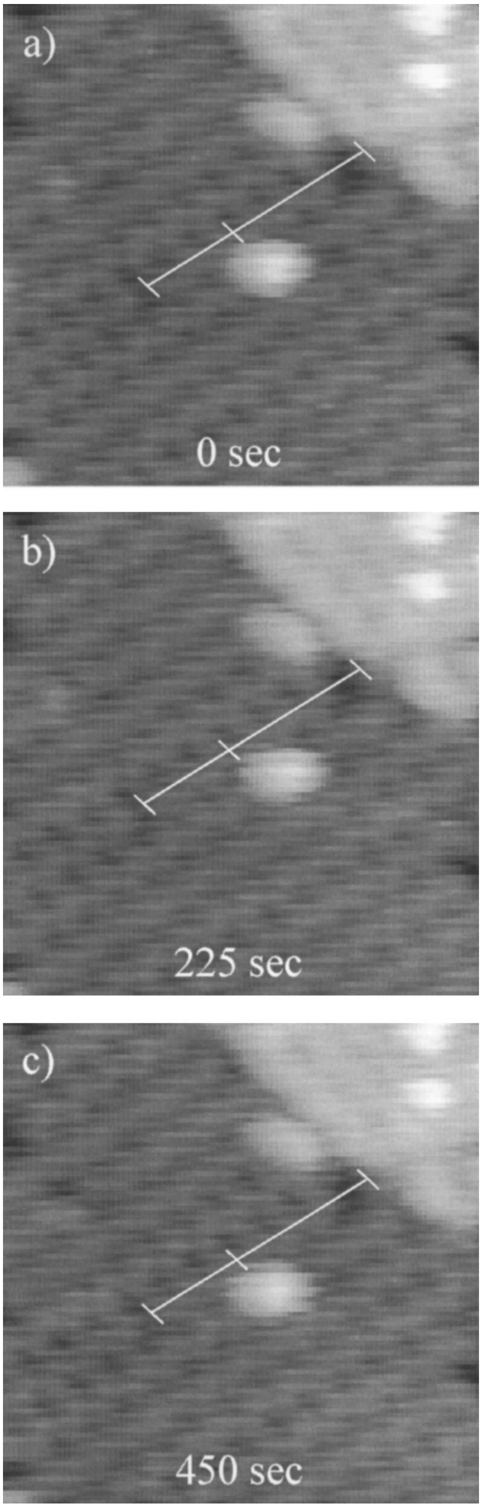

Fig. 3. Diffusing on-top Si dimer on strained Si(001) at room temperature. The marker indicates the ad-dimer starting position; sample bias −1.6 V, current 0.6 nA.

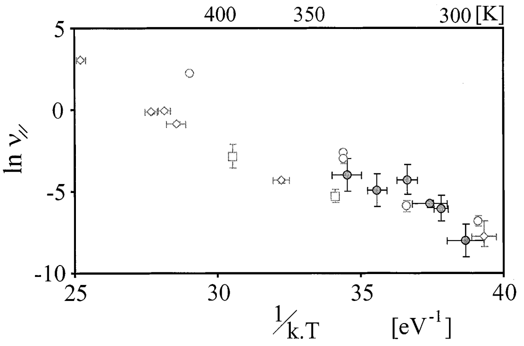

Fig. 5. *Along* row diffusion rates of a Si dimer on bare Si(001); Dijkkamp et al. [12] (open squares), Swartzentruber [13] (open circles), Krueger et al. [14] (open diamonds) and this work (gray circles).

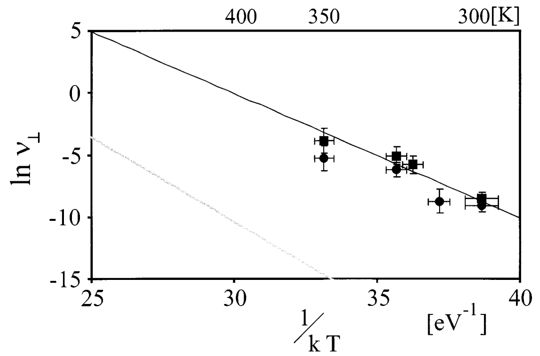

Fig. 6. On-top to trough diffusion rate of a Si dimer on strained Si(001) (black circles), on Ge(001) (black squares) and *across* row diffusion on bare Si(001) [15] (gray line).

Secondly, the *across* row diffusion of Si dimers on strained Si(001) and Ge(001) has been studied. A detailed analysis of many STM images of Si dimers on Ge(001) [16] has revealed that the probability of finding an isolated dimer in a trough position dominates over the probability of finding a dimer in an on-top position. In thermal equilibrium this would imply that the trough position has a lower energy than the on-top position. But since thermal equilibrium has probably not been established, a possible difference between diffusion barriers to and from a trough position has to be extracted from the average residence time. For Si dimers on Ge(001), the *across* row diffusion rate at room temperature has been estimated to be 10^{-4} Hz [17]. For Si dimers on bare Si(001), no across row diffusion is observed at room temperature. This is consistent with experiments performed by Borovsky et al. [15]. A diffusion barrier of at least 1.36 eV (attempt frequency $10^{13.2}$ Hz) has been found, which translates into a diffusion rate as low as 10^{-10} Hz at room temperature. Interestingly, we have found a number of *across* row diffusion events at room temperature for Si dimers on 4% *tensile* strained Si(001) surfaces. The estimated *across* row diffusion rate of 10^{-4} Hz is the same as for Si dimers on Ge(001).

To further investigate the diffusion rates for the *across* row direction, the rate for a jump from an on-top position to a trough position has been determined at different temperatures. The rates are determined by measuring the average residence time in the observed *across* row events. Fig. 6 shows Arrhenius plots of *across* row diffusion of Si dimers on strained Si(001) and on Ge(001). The large error bars are due to the limited number of observed events. The solid gray line refers to the value for Si on bare Si(001), with a diffusion barrier of 1.36 eV and an attempt frequency of $10^{13.2}$ Hz [15]. The rates for *across* row diffusion of Si on bare Si(001) are well below the rates of both Si on strained Si(001) and Si on Ge(001). The rates for Si on strained Si(001) are slightly below, but still comparable with Si on Ge(001). The slope of the black line [fit on Si on strained Si(001) and Ge(001)] indicates a lower diffusion barrier than for Si on bare Si(001). The *across* row diffusion barrier of Si ad-dimers on strained Si(001) and on Ge(001) is about 1.0 eV, assuming an attempt frequency of 10^{13} Hz.

Recollecting, the diffusion rate of Si dimers on 4% *tensile* strained Si(001) *along* the surface dimer rows is a factor of 10^2 lower than the rate on bare Ge(001), while the *across* row direction has a rate comparable with Si on Ge(001). This leads, for Si dimers on 4% *tensile* strained Si(001), to a diffusion anisotropy *along* and *across* the surface dimer rows of about 10 in the temperature range measured. This anisotropy is small compared with the anisotropy on bare Si(001) or Ge(001).

The influence of a 4% *tensile* strain on the *along* row diffusion rate of a Si dimer on Si(001) surface turns out to be small. The diffusion pathway of an ad-dimer *along* the substrate dimer row is shown by Borovsky et al. [27] to involve a dimer moving one atom at a time rather than moving as a unit. The dimer enters a weakly bonded state, while one atom moves ahead, so the two dimer atoms remain together during diffusion[2]. The highest energy barrier involved (the rate limiting step) for Si on Si(001) is the partial dissociation of the dimer, whereas recombination has a much lower barrier. The rate limiting step turns out to be not very receptive for an applied *tensile* strain.

In contrast to the *along* row direction, no dimer dissociation step has been predicted for *across* row diffusion [15,28]. In this direction, therefore, an influence of an applied strain may be expected. An enhancement of the *across* row diffusion rate for Si ad-dimers on a *tensile* strained Si(001) surface has indeed been found. At first sight this seems to be in disagreement with a decrease in diffusion rate predicted for *tensile* strained metal systems. But since the Si(001) surface is anisotropic, an applied strain may have a different effect on diffusion. The *across* row pathway involves the jump over a bridging site between two adjacent in-row surface dimers (from A/B to C/D or vice versa). The *tensile* strain *along* the dimer row direction results in an increase in the diffusion barrier similar to metal systems and probably in a decrease of the barrier height at the bridging site. The *tensile* strain in the direction *across* the dimer rows will result in an increase in barrier height at the same bridging site. Therefore the net barrier for diffusion *across* the surface dimer rows can either increase or decrease. Our experiments suggest that the overall effect is a decrease in barrier height.

In conclusion, the current work demonstrates that for semiconductor Group IV (001) surfaces there is no unique relation between lattice mismatch-induced *tensile* strain and the rate of surface diffusion. The strain influence is believed to be sensitive to the diffusion mechanism involved. The latter result is in marked contrast to metal surfaces where a *tensile* (*compressive*) strain lowers (enhances) the rate of surface diffusion.

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[2] Even if we assume that the dimer dissociates completely and the neighboring individual atoms both perform an uncorrelated 1D random walk, their expected reunion site is close to the dissociation site of the dimer. Our statistics do not allow us to discriminate between complete dissociation or diffusion as an unaltered unit for the dimer diffusion pathway.