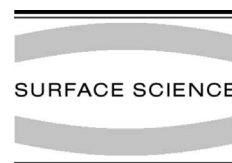




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# STM investigation of the initial adsorption stage of Bi on Si(1 0 0)-(2 × 1) and Ge(1 0 0)-(2 × 1) surfaces

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## Abstract

Scanning tunneling microscopy has been used to investigate the initial adsorption stage of Bi on Si(100) and Ge(100) surfaces at room temperature. The most favorable position for a Bi ad-dimer on both surfaces is the B-configuration (Bi ad-dimer positioned on-top of the substrate rows with its dimer bond aligned along the substrate dimer row direction). For Si(100) the A-type dimers (dimer bond aligned perpendicular to the substrate dimer row direction) occasionally rotate back and forth to a B-configuration. The diffusion rates of B-type and A-type dimers along the substrate row and the B–A, A–B rotations on Si(100) are extracted from an analysis of many sequences of STM images. Finally, it is shown that the presence of an attractive interaction between Bi ad-dimers (irrespective of their orientation) positioned on neighboring substrate dimer rows leads to the formation of local regions with a 2 × 2 reconstruction. © 2001 Published by Elsevier Science B.V.

**Keywords:** Scanning tunneling microscopy; Bismuth; Silicon; Germanium; Surface diffusion

## 1. Introduction

The growth of various types of overlayers on semiconductor surfaces has been widely investigated theoretically and experimentally for the past decades. The interaction of the group V elements such as As, Sb and Bi on Si(100) and Ge(100) surfaces is important in the light of use of these elements as surfactants in heteroepitaxy. To understand the role of these elements in heteroepitaxy one should investigate structural and electronic properties of (V group)/Si(Ge) interfaces, in detail.

Additionally, the creation of atomic wires for e.g. the Bi/Si(100) system under special conditions is another interesting point that justifies a detailed investigation of Bi adsorption on Si and Ge surfaces [1,2]. The initial stage of Bi adsorption on the Si(100)-(2 × 1) surface was shown to lead to island formation with 2 × 2 periodicity, where Bi ad-dimers are positioned on the substrate dimer rows with their dimer bonds aligned along the substrate dimer row direction (B position, Fig. 1) [3]. At a coverage ~0.5 ML Bi dimers start to occupy positions between the substrate rows. This eventually leads to the transformation of a 2 × 2 into a 2 × 1 periodicity (B and C position in Fig. 1) [1–3]. In contrast to Si and Ge ad-dimers on Si and Ge(100), A and D positions for Bi dimers have not

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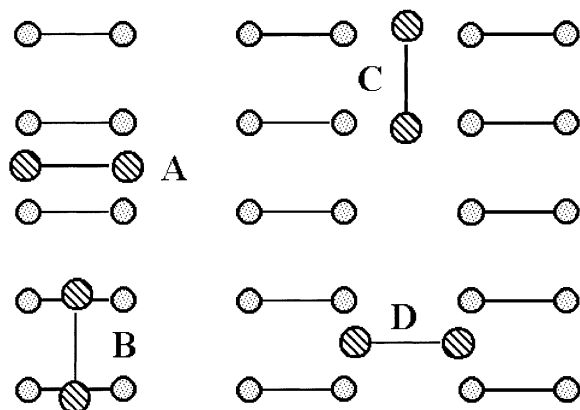


Fig. 1. Schematic diagram of the various possible adsorption sites for ad-dimers on the Si(100) and Ge(100) surfaces. A,B,C,D-adsorbate dimers.

been found. In the case of Bi on Si and Ge(100) surfaces, a detailed knowledge on the diffusion is absent. Meanwhile, the diffusion of Si and Ge ad-dimers on the Si(100) and Ge(100) surfaces has been studied in quite some detail [4–11]. In this paper it is our aim to study the adsorption as well as the diffusion of Bi ad-dimers on the semiconductor group IV (100) surfaces.

## 2. Experimental

The experiments with Si(100) samples were carried out in an ultra-high vacuum chamber with a base pressure below  $2 \times 10^{-10}$  Torr. The chamber was equipped with a scanning tunneling microscope [12], AES-analyzer and heater for a sample and a tip. The Si(100) samples were cut from a P-doped wafer (4.5  $\Omega$  cm). After chemical pretreatment it was outgassed for a few hours at 700°C with a subsequent annealing at 1200°C for 1 min. The Ge(100) samples were also outgassed for several hours in the UHV system. The final cleaning stage consisted of cycles of Argon ion bombardment and annealing at 800°C. After annealing the samples were cooled down at a rate less than 100°C/min. The absence of impurities on the sample was controlled by AES and STM. The treatment resulted in well-ordered Si(100) and

Ge(100) surfaces. Bi was deposited on the samples from a tungsten basket. The Bi coverage was calibrated through a quartz oscillator.

## 3. Results

We have adsorbed a small amount of Bi ( $\sim 0.05$  ML) on the Si(100) surface (Fig. 2). One can see that the bright spots are positioned on-top of the substrate dimer rows and that they are slightly elongated in the row direction. Moreover, by comparing the total number of these spots with the amount of deposited Bi we arrive at the conclusion that the bright spots are Bi dimers in the B-position, which agrees well with previous experiments [3]. In the case of Bi adsorption on Ge(100) (Fig. 3) also the B-position turns out to be the most favorable adsorption site. As it has been previously reported the position of Bi ad-dimers is not at random [3]. The existence of small areas with a local  $2 \times 2$  periodicity for Si(100) and even  $2 \times 1$  periodicity for Ge(100) indicate that some rearrangement must take place at room temperature (RT). Unfortunately, repeated scanning of the same area for a few minutes did not show significant evidence for Bi dimer diffusion. Meanwhile, during scanning the scan area slightly moved due to thermal drift and evidence for motion of some bright blobs has been observed in fresh areas that newly appeared in the image. This motion gradually ended after repeated scans and the images became more stable. The diffusive entity, which participates in such rapid diffusion, is shown in Fig. 4. In this figure one can see that the rapid diffusing entity is a Bi dimer oriented perpendicularly to silicon dimer rows and placed on top of substrate dimers rows (A-dimer). It should be pointed out that A-dimers are better resolved in STM images than B-dimers. In filled state images the A dimers appear as a double bright spot. In the case of Fig. 4(2) and (3) the images of the A-dimer looks like a cut spot. The cutting of the A-dimer is due to diffusion during imaging of the dimer. By using these position were cutting takes place we can determine the position as well as the diffusion rate of the dimer. One can finally see the transformation of the A-dimer into the more stable

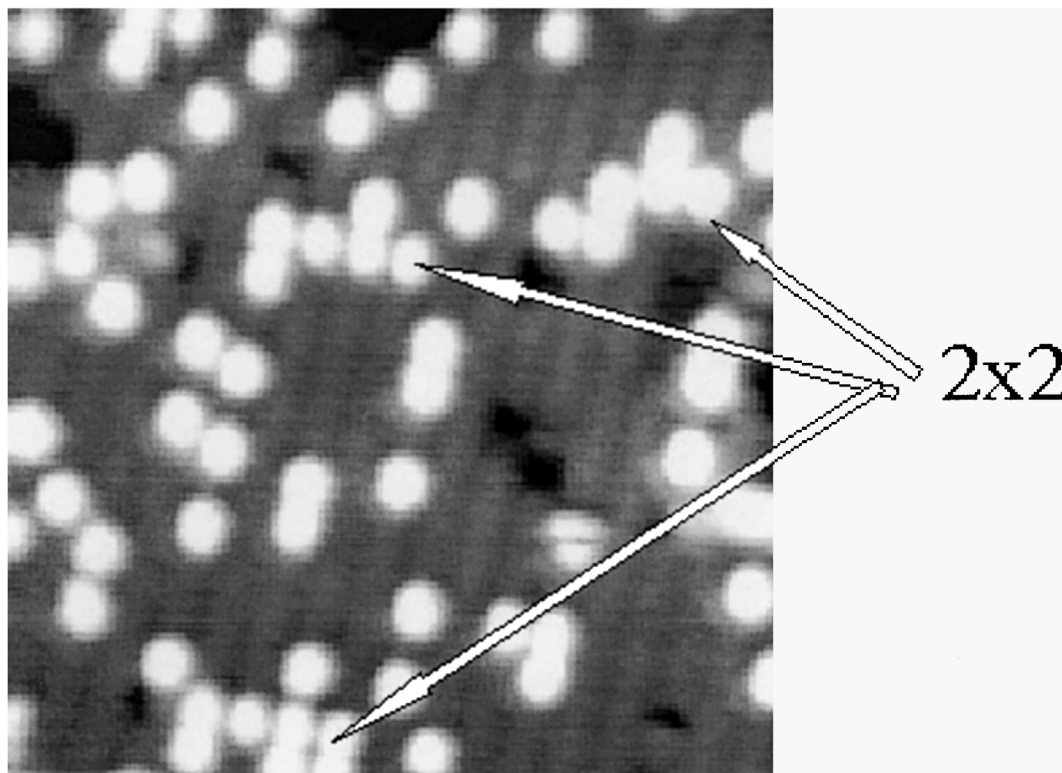


Fig. 2. STM-image ( $\sim 11 \times 11$  nm) of Bi adsorbed at RT on the Si(100) $2 \times 1$  surface ( $-2.0$  V, 46 pA). Bi adsorbs as B-dimers on substrate dimer rows with a local  $2 \times 2$  periodicity.

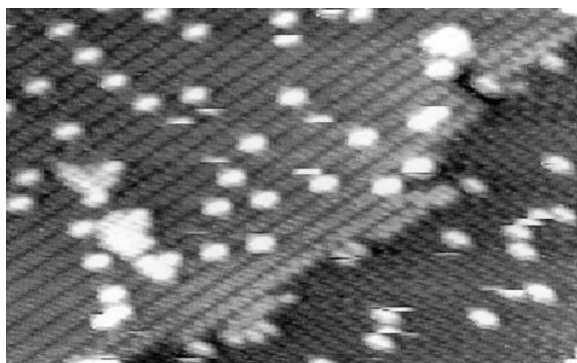


Fig. 3. STM-image of Bi/Ge(001). Isolated Bi ad-dimers are found in B-positions. Besides the isolated Bi ad-dimers also some small  $2 \times 1$  islands are observed. Scan area  $25 \times 16$  nm<sup>2</sup>. Sample bias  $-2$  V and 1 nA tunneling current.

B-dimer (Fig. 4(4)). An influence of the STM-tip as a stimulator, as has been observed for many systems [8,10], cannot be ruled out.

In order to study the diffusion of Bi dimers we have recorded comparatively larger areas of surface for a longer time than in the previous case and tried to find any evidence for displacement events of B dimers. And indeed, some B-type dimers changed their position. Besides the transformation from A-type dimers into more stable B-type dimers we only observed very rarely the conversion of B-type dimer into a less stable A-type dimer. Furthermore, we did not observe any event in which an on-top Bi ad-dimer jumps in a trough site or to an on-top site of an adjacent substrate dimer row.

On the base of the recorded sequences of STM-images, we have estimated the characteristic rates for the elementary diffusion processes on the Si(100) surface. Estimates for the diffusion and rotation rates have been made in two different ways. The first one is averaging of the time between successive events in the case when this time

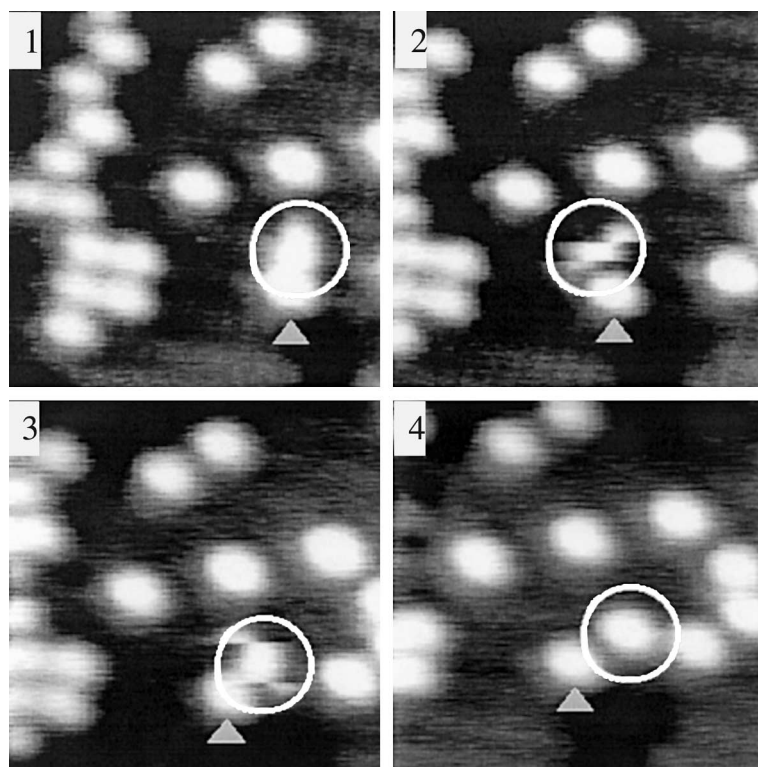


Fig. 4. Sequence of STM-images ( $\sim 6 \times 6$  nm) of the Bi/Si(100) $2 \times 1$  interface ( $-2.0$  V, 16 pA). Diffusion of Bi A-dimer and its transformation into B-dimer are shown.

lapse is much larger than the time lapse between successive images. This way of averaging is suitable for processes with very low rates. The second way is a careful analysis of individual images in the case the time lapse between successive events is smaller than the time period to obtain a single image (e.g. for A-type dimer diffusion). Because the diffusion of A-type dimers takes place in the direction of the substrate dimer rows, we chose the scanning direction close to the direction of the substrate dimer rows and made an estimate of the fast diffusion along the substrate dimer row by time averaging over A-type dimers that appear as “noncutted” features. For instance in Fig. 4(2), the A-type dimer stays at the same place for 10 scanning lines which correspond to a time lapse between hops of  $\sim 2$  s. Of course the latter approach is only appropriate in the case when the time of scanning a single line is lower than the time lapse between successive hops. We have also estimated

Table 1

Estimated hop frequency and activation energies for diffusion and mutual rotation (assuming the same attempt frequencies as for Si ad-dimers [8–10])

Type of transition	Estimated hop frequency (Hz)	Estimated activation energy (eV)
A–A	0.2	0.82 ( $\nu_0 = 10^{13}$ Hz)
B–B	$2.5 \times 10^{-5}$	1.05 ( $\nu_0 = 10^{13}$ Hz)
A–B	$3 \times 10^{-4}$	0.87 ( $\nu_0 = 10^{11}$ Hz)
B–A	$5 \times 10^{-7}$	1.04 ( $\nu_0 = 10^{11}$ Hz)

the activation energies for diffusion and rotation of A- and B-type dimers (Table 1). These estimates were made within the framework of Arrhenius behavior and under the assumption that the attempt frequencies of diffusion ( $10^{13}$  Hz) and for dimer rotation ( $10^{11}$  Hz) are the same as for Si ad-dimers on Si(100) [8–10]. The influence of an electric field (due to the STM) on the determination of activation energies is not investigated here

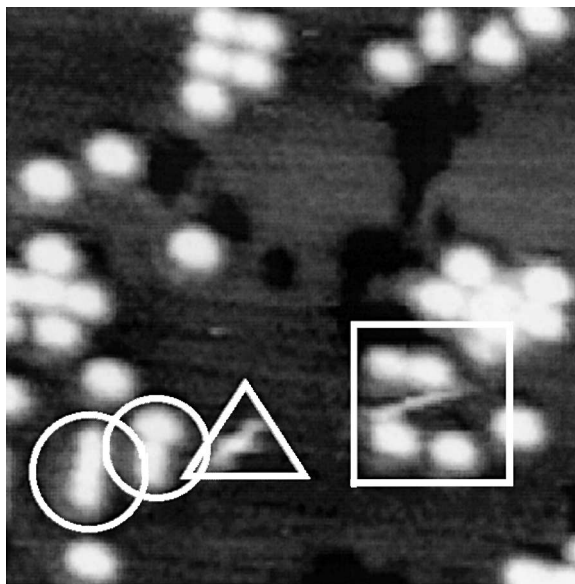


Fig. 5. Sequence of STM-images ( $\sim 10 \times 10$  nm) of the Bi/Si(100) $2 \times 1$  interface ( $-1.8$  V, 16 pA). A-dimers near A- and B-dimer in neighbor row are shown by circles. A free A-dimer is shown by triangle and an A-dimer between B-dimers in two neighbor rows is shown by square. Bi dimers in neighboring rows influence the Bi A-dimer diffusion.

but is expected to lead to different activation energies in general (at maximum  $\sim 0.1$  eV as has been found for Si ad-dimers on Si(100) [10]). By comparing the rotation rates of A–B and B–A as well as determination of relative population A vs. B we found a preference for the B-type adsorption site versus A-type adsorption site of  $\sim 0.2$  eV.

The following step of our investigation is to determine the influence of other Bi dimers on the diffusion of a Bi dimer. In Fig. 5. A-type dimers near A- and B-type dimers in the neighboring row are denoted by circles. One can see that the A-type dimer diffusion is remarkably inhibited as compared to an isolated A-type dimer (denoted by a triangle). This increase in the activation energy for diffusion of an A-type dimer near another adsorbed ad-dimer in a neighboring row is estimated to be  $\sim 100$  meV (assuming an attempt frequency of  $10^{13}$  Hz).

Another interesting observation (area within the square) is shown in Fig. 5: the A-dimer moves very rapidly (exhibiting jumps in practically each new scan line) in a region trapped between several

B-dimers in neighboring rows. The decrease in diffusion activation energy for this A dimer is estimated to be  $\sim 50$  meV.

This enhancement in surface diffusion is very important as it might explain the creation of a small areas of  $2 \times 2$  periodicity at RT. The influence of neighboring B-type Bi dimers in the same row on the diffusion has not been analyzed in detail but from a quick analysis of several sequences of STM-images it is found to be not very significant.

Also surface defects may affect surface diffusion. In Fig. 6 an image of a Bi/Si(100) surface containing quite some amount of defects is shown (the surface defects are mainly missing dimers and so-called  $1 + 2$  vacancies). For this surface, which contains a substantially amount of defects, more Bi dimers (denoted by circles) seem to be located in trough positions (C or D sites) as compared to more cleaner surfaces. A careful analysis of many STM images reveals that those trough C and D dimers can also rotate and diffuse. Moreover in the presence of defects Bi dimers can jump back and forth between on-top and trough sites. This phenomenon will promote the transition from a  $2 \times 2$

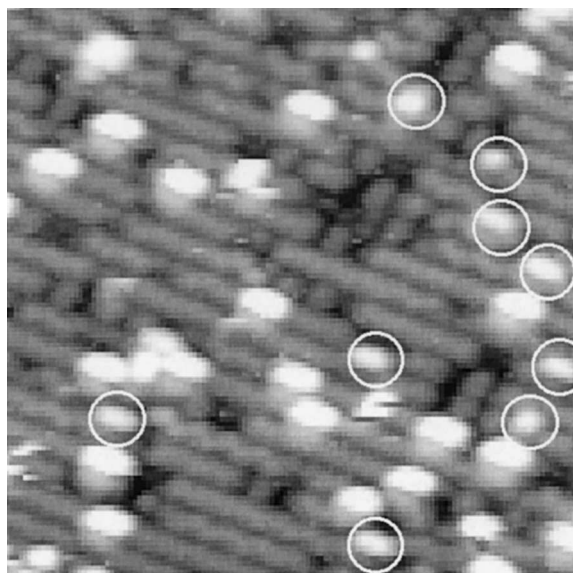


Fig. 6. STM-images ( $\sim 13 \times 13$  nm) of the Bi/Si(100) $2 \times 1$  interface with missing dimer defects on the surface ( $-2.0$  V, 196 pA). Bi dimers (mainly B-dimers) can be found between rows (circuits in the figure).

reconstruction to  $2 \times 1$  reconstruction at higher temperatures and/or higher Bi coverage.

#### 4. Conclusion

We have found that Bi dimers on the Si(100) $2 \times 1$  surface adsorb not only as B-type dimers, but occasionally also as more mobile and less stable A-type dimers. For Bi/Ge(100), however, only isolated B-type dimers were observed. On the base of a detailed analysis of several sequences of STM-images the diffusion rates of B-, A-type dimers and their mutual transformation rates were estimated. These rates are converted to activation energies by assuming that the attempt frequency is the same as for Si ad-dimers on Si(100), i.e.  $10^{13}$  Hz ( $10^{11}$  Hz for rotation). The mutual interaction between the Bi ad-dimers favors the formation of Bi islands with a  $2 \times 2$  structure.

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