Vacancy migration, adatom motion, and atomic bistability on the GaAs(110) surface studied by scanning tunneling microscopy

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In this article scanning tunneling microscopy studies of atomic motion of defects on the GaAs(110) surface at room temperature are reported. The slow dynamic behavior of vacancies and As adatoms can be resolved within a time scale of about one minute. The vacancies and As adatoms are observed to move preferably along the [$\bar{1}$10] direction, corresponding to a large anisotropy in the two-dimensional diffusion coefficients. We attribute such a large anisotropy to the energetics of atom migration in the presence of the GaAs(110) surface zigzag chain structure. Observations of As adatoms also indicate that they form linear chains along the zigzag chain. Finally, the fast dynamic behavior of atomic flip-flop action at a dual divacancy is discussed. The characteristic flip-flop time is estimated from the scanning speed and sampling frequency to be on the order of milliseconds.

Despite the extensive efforts at preparing perfect crystal surfaces for scientific research and technological applications, surface defects are inevitable. Short-range surface defects, e.g., surface vacancies and adatoms, are ubiquitous and will be present at any temperature above 0 K for thermodynamic reasons. Detailed knowledge of surface defects on the atomic level, particularly the real-space view of time-dependent behavior, is crucial for understanding various surface processes. In this article, we report scanning tunneling microscopy (STM) studies of atomic motion of vacancies and As adatoms on the cleaved GaAs(110) surface at room temperature.[1]

Typically, a cleaved GaAs(110) surface contains very few defects. Upon cleaving, the average terrace size is usually anywhere from a few hundred to a few thousand angstroms. Thus, large areas of perfect, defect-free crystal are easily and most often obtained. In the past, the low probability of defects has precluded the possibility of detailed defect studies on this surface. However, it is possible to create a high concentration of defects by purposely cleaving the sample in a certain way. During a "bad" cleave, a large amount of energy is introduced in a short period of time resulting in a surface free energy larger than the value at thermal equilibrium; however, due to the kinetic barrier at room temperature the high concentration of defects created may not revert back to the lowest free energy configuration at thermal equilibrium. This is similar to the process of surface quenching wherein morphologies which do not normally exist at room temperature due to thermodynamic reasons can be prepared for studies at room temperature.

Slow dynamic behavior of these defects can be resolved by STM within a time scale of about one minute, similar to that reported by others.[2–4] However, we will also show that in special cases, atomic motion can be resolved within a time scale of a few *milliseconds* corresponding to the time for the tip to scan over an atomic site. The former allows us to obtain information concerning defect motion within the range covered by the scan area of the STM while the latter provides an intriguing view of some interesting short-range behavior over an atomic site.

We focus our studies on two types of defects, namely, vacancies and adatoms which we identify as "As" adatoms. We have found that vacancies, including Ga (and As) vacancies and vacancies with both species missing, move primarily along the [$\bar{1}$10] direction, namely the direction of the GaAs zigzag chains. This motion along the [$\bar{1}$10] direction corresponds to a very large anisotropy in the two-dimensional diffusivity. Similar anisotropy in the atomic motion is observed for As-adatom chains. We interpret the large anisotropy as due to the potential barriers formed by the GaAs zigzag chains which confine the atomic motion along the [$\bar{1}$10] direction. These atomic motions are "slow" dynamics resolved by the STM within about one minute. The last one to be discussed is a "fast" time scale ($\approx$5–250 ms) atomic flip-flop being observed at a dual divacancy, namely, the vacancy with two pairs of Ga and As atoms missing.

Our experiments were performed in an ultrahigh vacuum STM system with a base pressure of 6×10^{-11} Torr or better. The samples were prepared from *n*-type GaAs wafers (Si doped, 1×10^{18} cm^{-3}) with wafer normal along the [001] direction. Sample size was typically 3 mm$\times$10 mm$\times$0.5 mm thick. A cleaving mark was made along the [$\bar{1}$10] direction by using a diamond-tipped scribe. Our samples were cleaved *in situ* by applying a force along the [001] direction. A surface cleaved in this way usually has a thin rough area which contains a high concentration of defects. Chemically etched tungsten tips were cleaned *in situ* by using the field emission method[5] on a freshly cleaved silicon or graphite surface. The STM tip was intentionally moved to particularly rough areas of the cleaved surfaces to observe a large number of defects. Typical tunneling currents were about 300–900 pA, and the tunneling voltages were between 2 and 3 V in magnitude for both polarities. All images were taken in the constant-current mode. Relative positions of Ga and As sublattices were determined from the dual-biasing mode where the tip bias polarity alternates between line scans.[6]

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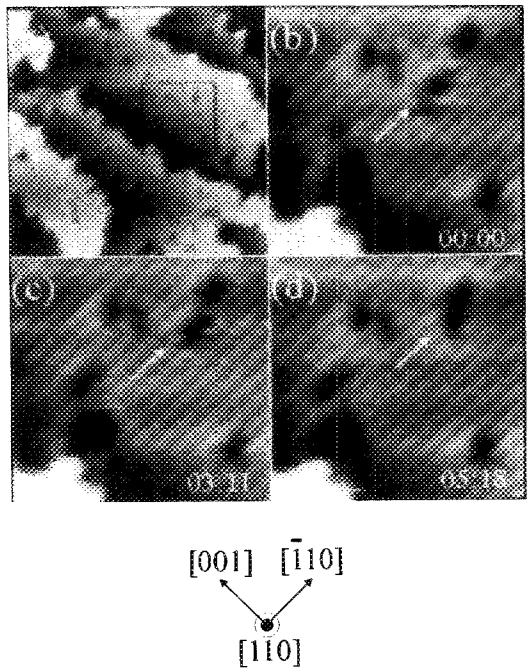

FIG. 1. (a) STM image, 260 Å×260 Å, of a cleaved *n*-GaAs(110) surface with the tip biased at +3 V and tunneling current of 900 pA. Many vacancies in this image show room temperature mobility. (b), (c), (d) One set of consecutive close-up images [$\Delta t \approx 2$ mins, scan area is 80 Å×80 Å, as indicated by a frame in Fig. 1(a)], which shows the merging of two vacancy clusters. White arrows are used to point out the moving vacancies. Elapsed time in minutes:seconds is indicated at the bottom of each image.

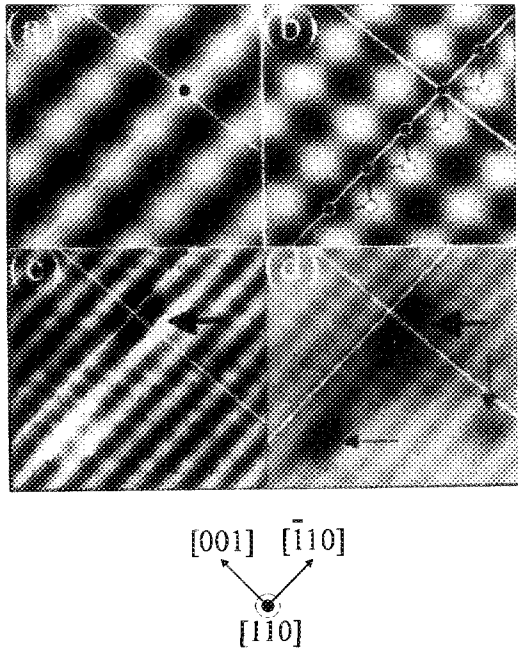

FIG. 2. (a), (b) Dual-biasing mode STM images of a perfect lattice region on the cleaved *n*-GaAs(110) surface with the tip biased at +2.75 V [(a), As sublattice] and −2.75 V [(b), Ga sublattice]. The tunneling current is 600 pA and the scan area is 22 Å×22 Å [the unit cell of the GaAs(110) surface is 4 Å×5.65 Å]. The cross hairs are used to show the relative positions of As and Ga sublattices. (c), (d) An example of a dual divacancy (two pairs of Ga and As atoms missing), a Ga vacancy (single Ga atom missing), and a Ga divacancy (two Ga atoms missing) with filled states, (c), imaged with tip biased at +2.94 V and empty states, (d), imaged with tip biased at −2.94 V. The tunneling current is 780 pA and the scan area is 50 Å×50 Å.

Figure 1(a) shows a STM image taken on the rough surface region. The image was acquired at a tip bias of +3 V and a tunneling current of 900 pA. As one can see, this image contains a large number of steps and vacancies. Many vacancies in this image show room temperature mobility. One example is shown in one set of consecutive images [Figs. 1(b)–1(d)]. As marked by the arrows, one observes that the indicated vacancy has moved along the [$\bar{1}$10] direction, namely the direction of the GaAs zigzag chains, by 5 Å over a time frame of 2 min.

The nature of the vacancies can be identified by performing polarity-dependent imaging. A filled-state image and an empty-state image on the GaAs(110) surface taken in the dual-biasing mode (atom-selective imaging) are shown in Figs. 2(a) and 2(b). Shown in Figs. 2(c) and 2(d) is an example of a dual divacancy and Ga vacancies where the empty-state image (tip negatively biased) shows three vacancy sites while the filled-state image (tip positively biased) shows only one. Interestingly, all three kinds of vacancies, namely Ga and As vacancies and vacancies with both species missing, show the same behavior of moving primarily along the [$\bar{1}$10] direction.

Our observation of vacancy migration, using different tips and samples, reveals that the direction of vacancy motion is primarily along the [$\bar{1}$10] direction. In a few rare cases, the moving direction of vacancy also involves a component along the [001] direction; however, the displacement along the [001] direction is always much smaller than the displacement along the [$\bar{1}$10] direction. This vacancy motion primarily along the [$\bar{1}$10] direction is equivalent to an enormously large anisotropy in the room temperature diffusion coefficient of vacancy along [$\bar{1}$10] versus along [001].

We next present the atomic motion of As adatoms on GaAs(110). Figures 3(a)–3(g) show a sequence of images acquired at positive tip biases (the time scale referenced to the first image is also labeled in each image). Figure 3(h) is the close-up image of the As-adatom chain enclosed by the dotted square in Fig. 3(g), and Fig. 3(i) is the corresponding schematic model for the relative positions of As adatoms and the GaAs zigzag chain. In Figs. 3(a), 3(b), and 3(g), one can observe a short chain of adatoms which are mostly two lattice sites apart along the [$\bar{1}$10] direction. Furthermore, these adatoms are located at the center of the As-sublattice unit cell, namely, they lie adjacent to the Ga atoms and most likely bond to them [Fig. 3(i)].[7] These adatoms are observed with a positive tip bias (namely, the filled-state image) while the negative tip bias shows a perfect adatom-free lattice. This evidence strongly suggests that these adatoms are As adatoms. Of course, the possibility of other chemical species cannot be completely ruled out.

The mobility of the As-adatom chains as observed in Figs. 3(a), 3(b), and 3(g) is derived from the fact that, in the same scan area, a chain of As adatoms moves two unit-cell lengths toward the top-right corner of the image

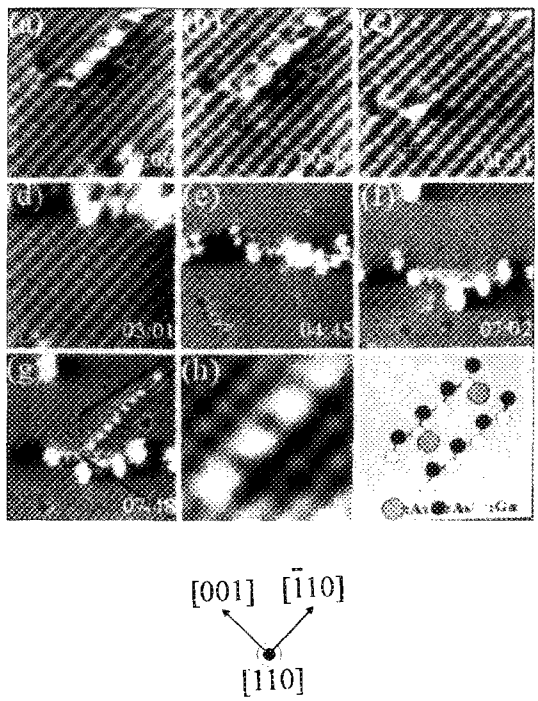

FIG. 3. (a)–(d) STM images of As-adatom motion on *n*-GaAs(110). The imaging area is on the lower terrace of (e)–(g). The As-adatom chain appears to move toward the step edge. The crosses " + " in the images are used as reference points. (e), (f) Larger area STM images which show the step edge, lower terrace and upper terrace of the GaAs(110) surface. In these images, the As-adatom chain disappears upon clustering on the step edge. These clusters often change shape and position with time. (g) The As-adatom chain reappears on the upper terrace after scanning for several minutes. (h) Close-up image of As-adatom chain enclosed by the dotted square in (g). (i) Schematic model for (h). Images (a)–(d) are 70 Å×70 Å. Images (e)–(g) are 135 Å ×135 Å. All images were acquired with the tip biased at + 3 V and a tunneling current of 800 pA. Elapsed time in minutes:seconds is indicated at the bottom of each image.

from Fig. 3(a) to Fig. 3(b) and moves out of the scan area in the next image (except one adatom). These images indicate that the direction of motion of this As-adatom chain is along the [$\bar{1}$10] direction and toward the step edge shown in Figs. 3(d)–3(f). Upon reaching the step edge, the As adatoms form clusters which change their position and shape in this series of images [Figs. 3(d)–3(g)], indicating a lateral mobility along the step edge. In Figs. 3(e)–3(g), one can see the adatom clusters on the left-hand side of the step edge have completely disappeared, and large atomic activity along the step edge is indicated by the clusters changing size. Furthermore, an adatom chain appears on the upper terrace in Fig. 3(g). We conclude that the most probable source for the adatom chain in Fig. 3(g) is the step edge. Although it is possible that the source of the adatom chain is outside of the imaged region, the step edge shown is the most likely due to the cause of the mobility as will be discussed below. Absolute volume comparison of adatom clusters is difficult since they are highly mobile along the step edge. This sequence of images illustrates the clustering and mobility of atoms along the step edge and the formation of highly mobile As-adatom chains along the [$\bar{1}$10] direction.

The mobility of adatoms along the [$\bar{1}$10] direction can be understood as they can run along the trench between the GaAs zigzag chains while the motion along the [001] direction requires that adatoms climb over the zigzag chains. We believe the observed mobility of As-adatom chains results from the electric field induced by the tip bias since those As-adatom chains are mobile with positive tip bias but stationary in the dual-biasing mode. However, we should mention that the observed moving direction (the [$\bar{1}$10] direction) of the adatoms is 45° from the scanning direction. Thus, even if the tip-induced field plays a role in assisting the adatom motion, the motion is still confined along the [$\bar{1}$10] direction.

In the case of vacancy migration, the tip–sample interaction does not seem to play the same role as in the motion of As-adatom chains.[8] According to our experimental observations, vacancy migration can be easily observed on areas with large vacancy population compared with those with small vacancy population. Therefore, the probability of observing vacancy migration is strongly correlated with the concentration of vacancies. We suggest that the extraordinarily large concentration of vacancies on some areas of the GaAs(110) surface created during the cleaving process represents a nonequilibrium situation at room temperature, which could be the major driving force for the vacancy movements. Further work is needed to conclusively identify the driving forces of vacancy migration on GaAs surfaces.

We now discuss the underlying mechanism for the observed anisotropic vacancy migration and As-adatom motion. In the consideration of energetics of atom migration, the atom prefers to move along the path which connects initial and final configurations with lowest potential barrier to cross. Because the GaAs zigzag chains represent a large potential barrier for atoms to move across,[9] the [$\bar{1}$10] direction is the preferred direction of atomic motion on the GaAs(110) surface. Consequently, despite the possibility that vacancy migration and adatom motion may have different driving mechanisms, the direction of motion is preferred along the direction of the GaAs zigzag chains.

Next, we discuss the atomic flip-flop action at a dual divacancy site. Figures 4(a) and 4(b) are two consecutive images acquired at a time difference of a few minutes. Because the tip was positively biased, these images correspond to the As sublattice. In these images, one group of atoms marked by the white arrow moves toward the step edge and forms ledge atoms to lower the total number of dangling bonds. A detailed analysis of the ledge atoms will be discussed elsewhere. Here, we will focus on the nature of the atomic flip-flop action. The atomic flip-flop phenomenon happens at a dual divacancy site (two pairs of Ga and As atoms missing) which is marked by the black arrow. Figures 4(c) and 4(d) are the close-up STM images corresponding to the same area in Figs. 4(a) and 4(b). At first sight, one may interpret the second image to show that an additional As atom has dropped into the dual divacancy site. However, close examination of the gray-scale images and line scans reveals that, in fact, it is a single As atom flipping back and forth between two equivalent sites.

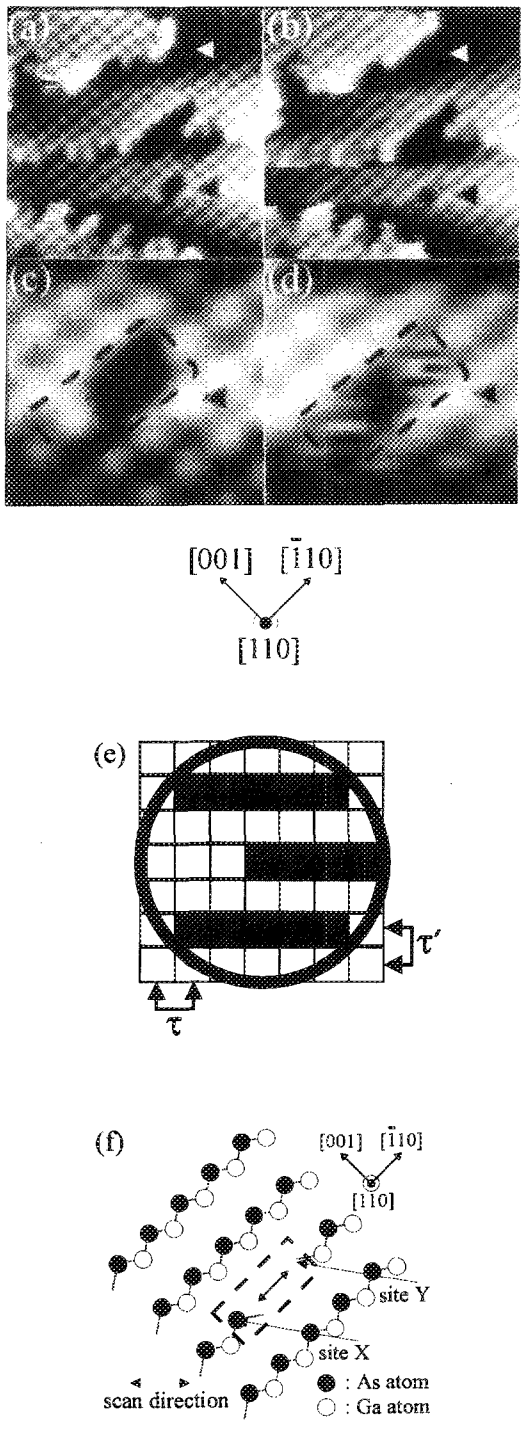

FIG. 4. (a) STM images, 90 Å×90 Å, of *n*-GaAs(110) surface. The white arrow points to the atoms near a step edge which rearrange themselves in the next image to a lower-energy configuration. The black arrow points to a dual divacancy site before the atomic flip-flop occurs. (b) STM image on the same area, a few minutes later, showing the occurrence of the atomic flip-flop. (c), (d) Close-up images near the dual divacancy site before and after the occurrence of the atomic flip-flop. All images were acquired with the tip biased at +3 V and a tunneling current of 600 pA. The tip scanning speed was 720 Å/s. (e) A schematic of the scanning area over a single atomic site *Y*. The white pixels indicate the presence of the As atom, and the black pixels indicate the absence of the As atom during the STM sampling time. The time interval between neighboring pixels is represented by τ and the time interval between two consecutive scan lines is represented by τ'. In our cases, τ is about 1 ms, and τ' is about 250 ms. (f) Schematic model showing the relative positions of Ga and As atoms in the region of the divacancy.

To illustrate the actual situation, Fig. 4(e) is used to simulate the actual tip scanning over atomic site *Y* [site *X* and site *Y* are labeled in Fig. 4(f)]. In this schematic drawing, the atomic site *Y* is represented by a circular region which is traversed by the tip approximately seven times during the entire scan. Due to the sampling frequency, the total number of sampling events within this atomic region was about 40. The white pixels indicate the presence of the As atom and the black pixels indicate the absence of the As atom. From the almost equal distribution of black and white pixels within this region, we conclude there is a fifty percent probability for observing the As atom on site *Y*. Similar analysis for site *X* yields the same conclusion. Furthermore, no As atom was ever detected between these two equivalent sites. To understand why these two sites are equivalent, consider Fig. 4(f), which shows the relative positions of the Ga and As atoms in the region of the dual divacancy. It is clear that the As atom bonding configurations are identical for both sites, *X* and *Y*. Therefore, we interpret the results to indicate an atomic flipping between the two sites with a certain characteristic frequency which is not synchronized with the scanning frequency. It is important to observe in the STM image that only in the dual divacancy region do we have this peculiar pattern of black and white "stripes." This observation allows us to rule out the possibility that we are seeing some kind of noise due to tip instability.

The flipping frequency of this atomic flip-flop can be estimated from the line scans of the STM image. As shown in Fig. 4(e), the black and white pixels in these line scans indicate whether an atom is observed or not on site *Y* during the sampling time. Thus, within the circular region, the average atomic occupancy time can be derived from the average length of continuous "stripes" composed of white pixels. The average atomic occupancy time is equal to the inverse of the flipping frequency. In this image (128×128 pixels), the time for the tip to scan across one pixel is about 1 ms, and the time difference between two neighboring line scans is 250 ms (STM image is acquired while scanning tip from left to right). From the length distribution of the black and white stripes in the line scans over this atomic site, we estimate that the inverse of the flipping frequency has a lower limit of 5 ms and an upper limit of 250 ms. The activation barrier height of the flip-flop action can be derived from the thermal activation scheme to be within the range from 0.62 to 0.72 eV. The detailed analysis will be presented elsewhere.[10]

In summary, we have used STM to study atomic motion of defects on GaAs(110) surfaces. For vacancies and As atoms, large diffusion anisotropy is found with both types of defects preferring to move along the [$\bar{1}$10] direction. This observation is attributed to the atomic energetics of atom migration on the GaAs(110) surface; defect motion along the [$\bar{1}$10] surface in the direction of the surface zigzag chains is energetically more favorable. In our STM studies, As adatoms are observed forming short mobile chains. Finally, a novel flip-flop action at a dual divacancy is observed which shows the potential of STM to study atomic processes on a millisecond time scale.

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