Scanning-Tunneling-Microscope Tip-Induced Migration of Vacancies on GaP(110)

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Scanning-tunning-microscope tip-induced migration of divacancies is observed on *n*-doped GaP(110). The motion occurs only at negative polarity of the tunneling voltage and along the [1$\bar{1}$0] direction, independent of the scanning direction, and is thus purely nonthermal. It is suggested that a field-induced reduction of the barrier for the migration initiates the motion. A quantitative analysis of the migration indicates long-lived excited states, consistent with charged trap states in doped semiconductors.

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The ability to resolve individual atoms over large fields of view makes the scanning tunneling microscope (STM) the ideal tool for investigations of the migration of atoms or defects. Such measurements can either be done "after the fact," in which a quenched-in distribution is observed and the thermally induced motion leading to this distribution is deduced [1], or "real time" in which actual motion is observed on the time scale of the scanning probe [2,3]. In the latter case there exists the possibility that the act of scanning affects the motion, as it is well known that manipulation of single atoms or strings of atoms is possible with the STM [4–6]. In this Letter we report a defect motion that is nonthermal and induced by the presence of the tip, the migration of divacancies on GaP(110) surfaces. Their motion appears to be due to an excited state created by the electric field of the tip. It is not due to a mechanical transport of atoms by the tip.

Gallium phosphide (GaP) can be cleaved in uhv (at a pressure of 1×10^{-8} Pa) to produce nearly perfect (110) surfaces. On the surfaces of *n*-doped GaP(110) (S doping between 5.6×10^{17} and 6.0×10^{17} cm^{-3}) defects that turn out to be divacancies (two missing P atoms) can be created by the tip at negative voltages applied on the sample relative to the tip. These divacancies were observed to migrate at room temperature when scanned at negative tunneling voltages in the range -2.6 to -3.8 V (Fig. 1). They do not, however, move when they are scanned at a positive tunneling voltage, nor do they migrate if the field is off. The divacancies moved nearly exclusively along the close-packed atomic rows in the [1$\bar{1}$0] direction, as only about 1% of the observed jumps had a component in the [001] direction. Thus the movement of the divacancies can be considered one dimensional.

The two defects imaged in Fig. 1 both move in the four consecutive images. The occupied dangling bonds localized at the P surface atoms dominate the images [7,8]. The images show 0.07 nm deep holes with the lateral extension of two adjacent dangling bond states, implying the presence of a double P vacancy. The divacancies migrate along the [1$\bar{1}$0] direction as single defects. If a divacancy moves by one lattice spacing a P atom must move over two lattice sites in the opposite direction. Such a motion is likely to occur with two (dissimilar) nearest-neighbor jumps. If the jump probability of the first jump were larger than that of the second jump, then the divacancies would dissociate into single vacancies. This is never observed, hence the jump probability of the first jump must govern the complete process and that of the second jump must be near unity. Hereafter, when we refer to a jump of length 1 of a divacancy, we mean its displacement by one lattice spacing, i.e., a jump of a P atom over two lattice spacings.

In order to quantify this migration, we continuously scanned over a number of defects, recording series of up to 250 consecutive images of 150×150 Å at 8 s/image (109 to 155 lines/image). Each line was scanned in about 70 ms and rescanned every 8 s. Typically there were between 4 and 10 defects in an image. The information presented here comes from more than 2500 observations of divacancies. At the magnification used the defects

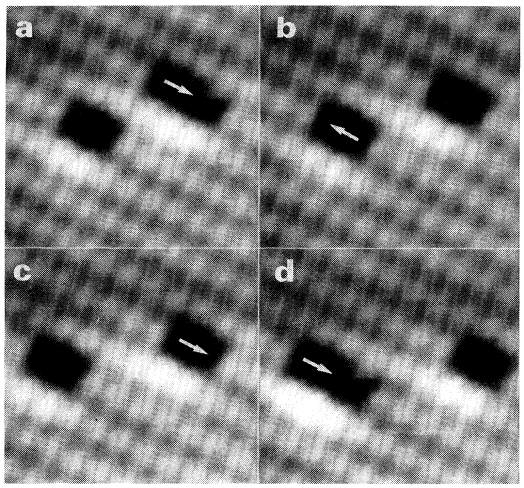

FIG. 1. Migration of double P vacancies. The scanning direction was from upper left to lower right. The arrows indicate the motion of the defect. Split defects in panels (a) and (d) imply that the jump occurred between one and the subsequent passes of the tip over the defect. Scale, 70×70 Å.

were up to 9 scan lines wide, so that we quite frequently observed "split" features or partially imaged defects, in which the jump occurred between one and subsequent passes of the tip over the defect [3,9]. Only that part of the defect that was scanned prior to the jump is recorded. The defect or a part of it might be seen again in the same STM image if it jumped into a position still to be scanned.

The observed migration cannot be dominated by thermally induced motion, because it could only be observed at negative tunneling voltages, while at positive voltages the defects were immobile. This dependence of the migration on the sign of the tunneling voltage and its correlation with the position of the tip require that the jumps be induced by the presence of the tip. At the temperature of the measurement, no thermal motion is discernible, i.e., rescanning an area after a period of time of no scanning showed no motion of the defects, implying that, at room temperature motion is negligible.

The measured distribution of defect displacements is shown in Fig. 2. The length of a displacement was measured from two successive images. The distribution of displacements is symmetric along the $\langle 110 \rangle$ direction. Independent of the scanning direction the migration occurred as frequently in the $[\bar{1}10]$ direction as in the $[1\bar{1}0]$ direction, confirming that the scanning direction does not affect the direction of the migration. This observation leads to our earlier stated conclusion that a mechanical transport by the tip is not the cause of the migration. Because thermal excitations are negligible, no jumps are expected between two images.

Most displacements were by one lattice spacing, but a significant number of longer displacements was also seen. The latter can be obtained by several consecutive jumps over one lattice spacing or by one longer jump. We reiterate that a displacement by one lattice spacing corresponds to the motion of one P atom over two lattice spacings. In analogy, a divacancy displacement of length 2 or 3 is obtained by the migration of a train of two or three P atoms over two lattice spacings, respectively. For a long jump, e.g., three cars in the train are coupled, while for a series of short jumps the cars are decoupled and each atom makes its migration independent of the others. To distinguish between these two possibilities, we calculated the probability of having a displacement of length n by summing over all possible jump paths and lengths up to three lattice spacings. The number of displacements of length n, $N(n)$, can be written [10]

$$N(n) = N_0 \left\{ \sum_{k,j} p_{3k}(\gamma) p_{2j}(\beta) p_{n-2j-3k}(\alpha) \right\}, \qquad (1)$$

with $p_i(\delta) = \exp(-\delta) I_i(\delta)$ being the probability of a displacement of length i ($i \in \{n,j,k\}$) with the jump probability δ ($\delta \in \{\alpha,\beta,\gamma\}$) per scan cycle (passes of the tip over the defect). α, β, and γ are the probabilities per scan cycle of jumps over one, two, and three lattice spacings, respectively. The magnitudes of these constants in thermally produced diffusion are fixed by properties of the crystal and by the temperatures; here the magnitude of the bias voltage or current can also affect them. I_i is the modified Bessel function. Symmetric jump probabilities in both directions along the close-packed rows were assumed. Furthermore the independence of each jump is assumed in Eq. (1).

Simulation a in Fig. 2, allowing only jumps over one lattice spacing, describes well the measured number of displacements over one lattice spacing, but deviates considerably for longer displacements from the measured distribution. Simulation c, including jump lengths up to three lattice spacings, agrees well with the measured distribution. The jump probabilities used for the simulation are $\alpha = 0.16 \pm 0.02$, $\beta = 0.018 \pm 0.006$, and $\gamma = 0.0054 \pm 0.003$ per scan cycle for jumps over one, two, and three lattice spacings, respectively. About 87% of all jumps occurred over one lattice spacing, the rest being excess probabilities of longer jumps, which decrease exponentially with the jump length. One can think of the tip exciting a train of 1, 2, 3, or more P atoms to move in a coherent fashion with some set of probabilities.

One can ask at this stage if the displacements of a particular divacancy are in any way correlated. The simplest assumption is that they are statistically dependent. The probability that a divacancy that has just jumped survives immobile s scan cycles before it jumps again is $P(s) = p(1-p)^{s-1}$ and an exponential dependence is expected ($p = \alpha + \beta + \gamma$). If there are two (or a family of) processes with different jump rates, the exponential decay will have different slopes. Figure 3 shows that for low values of scan cycles the number of divacancies having repeated jumps lies above the exponential curve (dashed line) expected for statistically independent events, suggesting that there is a positive correlation for repeated jumps of divacancies that have recently jumped.

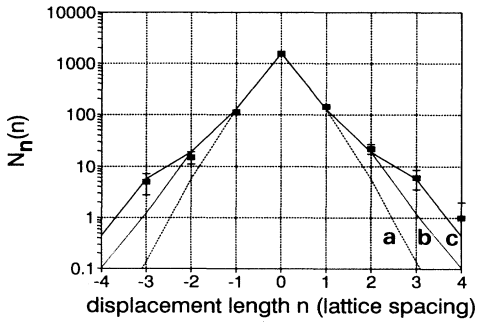

FIG. 2. Measured frequency distribution $N(n)$ of displacements. Displacements with negative lengths were oriented in the $[1\bar{1}0]$ direction. The lines a, b, and c are simulations of the measured data using Eq. (1), assuming divacancy jump lengths of one, up to two, and up to three lattice spacings, respectively. Data were obtained at a bias of -2.8 V and a tunnel current of 0.4 nA in the constant-tunnel-current mode.

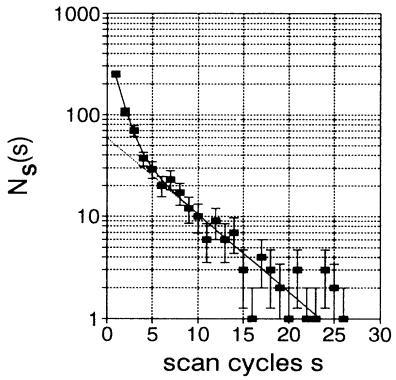

FIG. 3. Measured frequency distribution of the number of scan cycles, $N(s)$, between consecutive jumps of a defect. For statistically independent jumps an exponential curve is expected (dashed line). The solid line is calculated using a model of statistically independent jumps of two defect states with different jump probabilities. Bias and current are the same as in Fig. 2.

Figure 3 can be explained by assuming that in addition to a ground state of the defects there exists a second defect state that has a higher jump probability. The solid line in Fig. 3 shows a fit to the data using a model of two defect states with different jump probabilities (p_g and p_c) and statistically independent jumps:

$$N(s) = N_0[c_g p_g (1-p_g)^{s-1} + (1-c_g) p_e (1-p_e)^{s-1}], \quad (2)$$

where $N(s)$ is the number of scan cycles between consecutive jumps of a defect. The values of p_e and p_g are 0.6 and 0.16 per scan cycle, respectively, if the jumps are assumed to be statistically independent. c_g was found to be 0.5. This value might be interpreted as the probability that correlates the two defect states. If a defect has jumped, it has a 50% probability after the jump of being in each of the two states. Even though the data can be fitted with two defect states it may be physically reasonable to expect a family of states. The data can, of course, also be fitted with more states.

Finally, we found evidence for a correlation of the jump probability with the length of a preceding displacement of the defect (i.e., the length of the train). Figure 4 shows that the probability of having another jump increases with increasing displacement length of the previous jump. This correlation implies that the relative occurrence of the state with the higher jump rate increases with the length of the preceding displacement. Within the error bars, there is no correlation of jump direction with that of the previous jump. This lack of correlation of jump direction speaks against a possible influence of some intrinsic feature like a dopant atom. One might expect a negative correlation of jump directions if there were such an influence, i.e., an increasing energy of the defect as it moves farther from the extrinsic feature, and thus a "pulling back" on the defect.

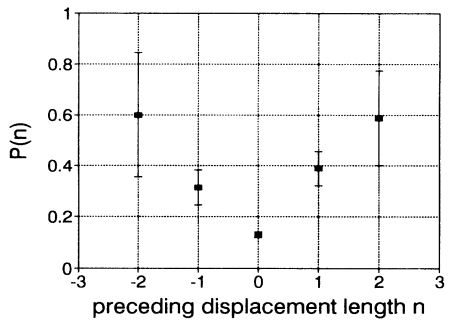

FIG. 4. Probability $P(n)$ of a displacement of a divacancy as a function of the length n of its preceding displacement. Bias and current are the same as in Fig. 2.

A number of possible models suggest themselves to explain these results, but most can be easily eliminated. A mechanical transport by the tip can be eliminated, as we have already stated, because the migration was found to be independent of the scanning direction. Tunneling of atoms enhanced by a tip-induced bending of bulk bands, without the presence of antibonding defect states in the gap, also cannot explain our observations, since such migration should occur for both polarities. Similarly, localizing heating of the surface due to the high current density, although it certainly exists, would enhance the migration at both polarities.

Energy injection into the defect by the presence of the tip can induce a migration. The voltage dependence suggests that this injection can be accomplished by the electric field of the tip. Calculations [11] and experiments [4,6] demonstrate that a field-induced transfer of atoms toward the tip can exist. A transfer of P atoms toward the tip was also observed on GaP(110) at negative voltages [12]. If the field is too weak to transfer atoms to the tip, they may nevertheless be moved a small distance out of their regular sites as the tip passes [13]. This is equivalent to an injection of energy. After the tip passes the defect, the atoms relax, but this additional energy may allow them to overcome the potential barrier holding them in a site and allow them to migrate. Longer jumps and the positive correlation of repeat jumps after a longer jump would then reflect a higher injection of energy.

A nearly equivalent picture results if the atoms attain a net charge through the passing of the tip as suggested by field ion microscopy measurements [14]. A net charge can be quite straightforwardly induced if there exists an unfilled (antibonding) state associated with the defect. The appropriate bias can bend the bands sufficiently to populate such states partially. This net charge can cause a lowering of the barrier for jumps and decay relatively slowly [15,16], leading to enhanced repeat jumps. A larger charge then leads to larger jumps and a higher correlation for repeat jumps. It has been theoretically

shown that atom migration can occur via succession of changes in the defect charge [17].

The one-dimensional nature of the migration can be simply explained in terms of different magnitudes of migration barrier in different directions. In the jump direction the lattice constant is a factor of $2^{-0.5}$ shorter than in the [001] direction, leading in the picture of the ballistic model for atomic migration [18] to a barrier of roughly half the height as compared to the barrier across the close-packed rows.

We conclude that the migration of divacancies on *n*-doped GaP(110) surfaces is induced by the tip because it depends on the polarity of the tunneling voltage and the jumps are correlated with the position of the tip. The one-dimensional migration and symmetric distribution of displacements makes possible a calculation of the probabilities of long jumps. They decreased exponentially with the jump length. A correlation exists between successive jumps of a divacancy: The probability for a repeated jump is higher if the divacancy jumped recently, suggesting long-lived charge states induced by the tip. A field-induced charge or energy injection is used as a possible model for the induction mechanism of the migration.

We have shown the possibility of measuring quantitatively jump length distributions to deduce detailed information on the nature of tip-surface interactions in STM. In this particular system, tip-induced motion completely dominates thermal motion at room temperature. Because the possibility of a tip contribution to motion exists in all real-time STM experiments of surface dynamics processes, it becomes necessary to separate out tip-induced from thermally induced motion. Experiments on this surface at higher temperatures are in progress with the goal of providing a quantitative separation of tip-induced and possible thermal motion.

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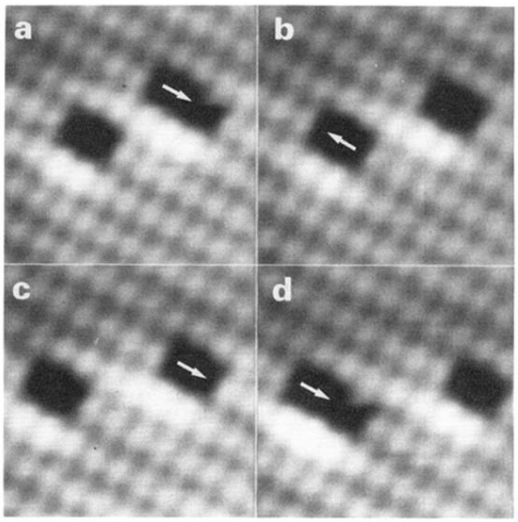

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