Colloquium: Time-resolved scanning tunneling microscopy

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Scanning tunneling microscopy has revolutionized our ability to image, study, and manipulate solid surfaces on the size scale of atoms. One important limitation of the scanning tunneling microscope (STM) is, however, its poor time resolution. Recording a standard image with a STM typically takes about a fraction of a second for a fast scanning STM to several tens of seconds for a standard STM. The time resolution of a STM can, however, be significantly enhanced by at least several orders of magnitude. Here various methods are reviewed that are applied in order to significantly improve the time resolution of STM. These methods include high-speed or video STM, atom-tracking STM, and monitoring of the open feedback loop current or closed feedback loop z -piezo-voltage signals as a function of time. An analysis of the time-resolved STM data allows one to map out the potential landscape of the system under study.

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I. INTRODUCTION

In the early 1980s [Binnig and Rohrer \(1982\)](#) invented a novel type of microscope, which they called scanning tunneling microscope (STM). The STM has an unparalleled spatial resolution. The ability of the STM to reveal images of individual atoms and molecules has resulted in a wealth of exciting discoveries and developments. Shortly after this major discovery Binnig and Rohrer were awarded with the Nobel prize in physics. They shared this Nobel prize with Ruska, who developed in the early 1930s the electron microscope ([Knoll and Ruska, 1932](#)). Until the 1930s microscopy relied on optical methods with a spatial resolution that was limited by Abbé's diffraction limit, i.e., $\sim 1 \mu\text{m}$. Ruska showed that by using high energy electrons rather than photons a much higher resolution could be obtained. Despite the strongly improved spatial resolution of Ruska's electron microscope, it was Müller who obtained, in the early 1950s, the first atomically resolved images of the apex of a sharp tip by using field ion microscopy ([Müller, 1951](#)).

The operation principle of STM is based on a quantum-mechanical phenomenon referred to as “tunneling.” When a sharp tip is placed less than 1 nm distance from a conducting sample and a voltage is applied between the sample and the tip, the electrons can tunnel through the vacuum barrier. The tunneling current de-

pends strongly on the overlap of the wave functions of the tip and the surface and thus on the distance between tip and surface. In the standard imaging process, the tip scans over the surface and a feedback system attempts to keep the tunneling current constant by varying the distance z between tip and surface. This mode of imaging is most frequently used and is denoted as “constant-current topography” mode [see Fig. 1(a)]. The z -piezo regulation voltage is recorded during scanning. Usually, it is converted to a height and represented by a gray level image. The bright areas correspond to protrusions on the substrate and the darker ones to depressions. For very flat substrates and small scanning areas, it is also possible to keep the height constant and measure the tunneling current during scanning [see Fig. 1(b)]. This mode is referred as “constant-height topography” mode. Nowadays STMs are commercially available and STM images with atomic resolution can be routinely obtained. The key reason that STM is such a powerful technique is that its operation involves tunneling electrons. The interaction of these tunneling electrons with electronic states and nuclear motion allows us to image, manipu-

FIG. 1. (Color online) Schematic representations of the two scanning modes in STM: (a) constant-current topography mode and (b) constant-height topography mode. In (a) the tunneling current is kept constant by varying the tip-surface separation. The z -piezo regulation voltage is recorded and converted to a height. In (b) the tunneling current is measured at a constant height. The tunneling current depends on the tip-surface separation.

late, spectroscopically characterize, dissociate, and form bonds between atoms.

Although the strengths of the STM are obvious, there are also a number of drawbacks of the technique, such as the relatively long image recording time and the limited control over the most crucial part of the microscope, namely, the tip.

In this Colloquium we review and discuss the rapid developments in the field of high time resolution STM. We first introduce the most straightforward and brute force solution, namely, high-speed scanning tunneling microscopy. In the main part we address an attractive alternative approach, where with a standard STM a temporal resolution down to 10–100 μs can be achieved. In this approach the tunneling current is measured as a function of time with the feedback loop switched off. This mode allows one to study relatively fast dynamical processes at a predefined position of the surface. Processes such as conformational changes of an individual molecule, atom attachment or detachment at a step edge, atom or vacancy diffusion, and flipping or rotation of a dimer can be studied in this mode. These types of measurements require of course a stable microscope that exhibits virtually no drift on a time scale of the open-loop experiment itself.

It should be mentioned here that the name time-resolved scanning tunneling microscopy was first used for the combination of STM with (quantum) optical techniques (Hamers and Cahill, 1991; Weiss *et al.*, 1995; Feldstein *et al.*, 1996; Groeneveld and van Kempen, 1996; Freeman *et al.*, 1997; Gerstner *et al.*, 2000; Khusnatdinov *et al.*, 2000; Takeuchi *et al.*, 2002; Terada *et al.*, 2007). The high spatial resolution of the STM and the high temporal resolution offered by ultrashort laser pulses enable high bandwidth measurements based on the pump-probe technique. The ultimate aim of this technique was to achieve simultaneously unprecedented spatial and temporal resolutions. It is, however, experimentally difficult to obtain a high spatial resolution because (1) the light should be coupled efficiently in the tunneling junction and (2) coupling of light in the tunneling junction usually leads to power dissipation and, hence, to thermal drift, which hinders high quality STM measurements.

II. HIGH-SPEED SCANNING TUNNELING MICROSCOPY

Dynamic processes on surfaces, e.g., atom diffusion, coarsening, or roughening, play a crucial role in many technological relevant areas, such as crystal growth, etching, and catalysis. A prerequisite for visualizing dynamic phenomena on surfaces is the ability to acquire sufficient temporal resolution, i.e., to collect STM images at a sufficiently high rate. The typical time to record a single image with a conventional STM is rather poor: it takes about 1 min to acquire a 400×400 pixels STM image. Such a time resolution is sufficient in case that the elementary process, i.e., atom or vacancy diffusion, occurs on approximately the same time scale. However, many processes occur on a much faster time scale and

FIG. 2. Three $83 \times 14 \text{ nm}^2$ high-speed STM images at 130 K, showing a step on the Cu(1 1 1) surface partly covered with indium atoms. Indium atoms that are deposited on a Cu(001) surface are embedded in the first layer of the surface. At room temperature the indium atoms are mostly incorporated through steps. Between (a) and (b) two of the indium rows [encircled in image (a)], which decorate the kinks along the step, are exchanging indium atoms. (c) The situation where several indium atoms have moved from the leftmost of the two rows to the right row. Time per image is 0.64 s, with sample bias of -2.083 V , and tunneling current of 0.1 nA . From van Gastel *et al.*, 2004.

are therefore not accessible with a standard STM.

For one-dimensional diffusion processes, such as the motion of a step edge or the preferential diffusion along one of the high-symmetry directions of a crystal, one can repeatedly scan the same line(s) and thus obtain a time versus position image with a time resolution in the range from 50 to 250 ms (Poensgen *et al.*, 1992; Kitamura *et al.*, 1993; Hoogeman *et al.*, 2000; Komeda *et al.*, 2002; Lyubnitsky *et al.*, 2002; Yoshida *et al.*, 2002). However, in order to study two-dimensional surface processes with a higher than conventional time resolution one needs to modify the STM quite substantially.

Several research groups have shown that, with an optimized mechanical construction and electronics, STM images can be recorded sequentially at approximately 1–100 frames per second (Linderöth *et al.*, 1997; Wintterlin *et al.*, 1997; Laegsgaard *et al.*, 2001; Besenbacher *et al.*, 2005; Rost *et al.*, 2005). These video STMs have a rigid and compact design in order to achieve the required high mechanical resonance frequency. In addition, a high bandwidth *IV* converter, fast analog-to-digital converters, and fast feedback electronics are used. In order to enhance the maximum scan speed even more Rost *et al.* (2005) implemented a hybrid mode between the well-known constant-height and constant-current modes. This hybrid mode also leads to a better resolution at lower scanning speeds. In addition, in order to achieve fast data transfer they developed a home-built bus structure.

As an illustrative example we show a sequence of images recorded with such a high-speed microscope (Fig. 2). The images show the diffusion of indium atoms in the In/Cu(1 1 1) system. Besides the fact that several laboratories around the world have built well-operating high-speed STMs, there are yet less cumbersome techniques available which improve the time resolution of conventional STMs significantly.

FIG. 3. (Color online) Schematic representation of the atom-tracking mode. The tip is dithered above the adsorbed atom in (a) and the lateral feedback [shown schematically in (b)] responds to the local slope, forcing the tip to climb uphill. For example, when the tip is offset to the left, the slope is positive and the tip is pushed back to the right.

III. TIME-RESOLVED SCANNING TUNNELING MICROSCOPY

A. Atom-tracking scanning tunneling microscopy

Since the early 1990s several research groups have explored the possibility of using STM to visualize dynamic processes on surfaces, such as atom diffusion, step fluctuations, and vacancy diffusion. An important limitation at that time was the poor time resolution of STM. The cutoff frequency of the feedback loop is usually of the order of a few kHz. The latter implies that dynamic processes that occur on a time scale of a millisecond or less are averaged out in the scanning process. In the mid-1990s, however, Swartzentruber (1996) introduced a technique with an improved time resolution that he called atom-tracking scanning tunneling microscopy.

Atom-tracking scanning tunneling microscopy relies on a tracking procedure that was put forward earlier by Pohl and Möller in the late 1980s (Pohl and Möller, 1988). In atom tracking the STM tip is locked onto a preselected atom or vacancy using two-dimensional feedback. The lateral feedback is accomplished by imposing a circular motion to the STM tip [see Fig. 3(a)]. This circular motion is generally a few angstroms in radius at a frequency higher than the cutoff frequency of the z -feedback electronics. A lock-in amplifier measures the derivative of the tunnel current with respect to the lateral coordinates x and y [see Fig. 3(b)]. These derivatives are passed on to independent x and y integrating feedback circuits that maintain a position of zero local slope (that is, on top of the atom). The net result of the lateral feedback is to force the STM tip to continuously climb uphill, following the local surface gradient and remaining at the top of the atom. By a simple inversion of the phases of the x - and y -feedback circuits, the atom

FIG. 4. (Color online) STM images ($4 \times 3 \text{ nm}^2$) of a Si(001) surface with a Si ad-dimer with its dimer bond aligned (a) parallel or (b) perpendicular to the dimer bonds of the underlying substrate dimer row. In (c) the measured z signal is shown as a function of time. The transitions between A and B positions show up as sharp changes in the measured z signal. From Swartzentruber *et al.*, 1996.

tracker can be forced to run downhill in order to lock onto a vacancy. In the atom-tracking mode, the STM spends all of its time measuring the kinetics of the selected atom, molecule, or vacancy instead of acquiring a two-dimensional image of its neighborhood. The data collection thus shrinks from a two-dimensional matrix to a continuous single point, i.e., zero-dimensional, data set. Hence, by tracking individual atoms, vacancies, or small clusters directly, the ability of the STM to measure dynamic events is increased by a factor of 10^3 as compared to conventional STM imaging techniques (Swartzentruber, 1996; Zandvliet *et al.*, 2001). Rather than this electronic approach to track a preselected surface feature, the tracking option can also be implemented by a software program. Stipe *et al.* (1997) used this software tracking option to reversibly displace Si atoms on a Si(111)-(7 $\times$ 7) surface.

The strength of the atom-tracking technique has been illustrated by an experiment performed by Borovsky, Krueger, and Ganz (1999). They showed that Si dimers diffusing along the substrate dimer rows of Si(001) always hop to nearest-neighbor sites. This strongly suggests that the on-top dimers remain bound during diffusion. The same experiment showed that dimer diffusion in the troughs of the Si(001) substrate is quite different. In the valleys, dimers execute double and triple jumps indicating that the dimer bond breaks and the two atoms move nearly independently along the trough until they meet again and recombine into a dimer.

In another landmark experiment in this respect the rotation of a Si ad-dimer on a Si(001) substrate dimer row was tracked. Si ad-dimers can have their dimer bond aligned in a direction either parallel (A) or perpendicular (B) to the dimer bonds of the underlying substrate dimer row. The presence of these two stable configurations is found in conventional STM images [see Figs. 4(a) and 4(b)]. Bedrossian (1995) and Zhang *et al.* (1995) found that the thermally induced rotational transition process occurs on the time scale of seconds at

room temperature. Rather than collecting a series of consecutive images Swartzentruber, Smith, and Jónsson (1996) monitored the rotation of an adsorbed silicon dimer on a dimerized Si(001) surface by recording z -piezo-voltage traces as a function of time [see Fig. 4(c)]. The two stable configurations have a different z -feedback position because of their structural and electronic structure differences. In the A configuration the ad-dimer is about 0.015 nm closer to the surface than in the B configuration. Therefore, the state of the dimer is simply reflected in the z -feedback position as a function of time. At room temperature, the adsorbed dimer rotates back and forth between the orthogonal B and A states on a time scale of several seconds. The dimer has a higher probability of being in state B, a consequence of that configuration's lower bound-state energy. The different transition rates for the A and B states are reflected in their residence times, the length of time spent in a given state before making a transition. The ratio of these averaged residence times immediately gives the energy difference between both states provided that the attempt frequencies of both states are same. If the latter condition is not satisfied, one should measure the temperature dependence of the residence times. By plotting the logarithm of the averaged residence time versus the reciprocal temperature the attempt frequency and the activation barrier can be determined.

Besides the above-mentioned advantages of the atom tracker there are also a number of disadvantages. First, during atom tracking the STM tip spends all of its time in direct proximity of the object under study. Since the electric fields and current densities can be large, the possibility arises that the tunneling process itself can affect the measurement of the activation or diffusion barriers. By systematically changing the applied bias and the tip-sample distance, one can systematically vary the tip-induced electric field in both magnitude and direction. The effect of the tunneling conditions, such as electric field and tunnel current dependencies of adsorbed Si dimer dynamics on Si(001), has been studied by Carpinelli and Swartzentruber (1998) using atom tracking. They found that the electric field has little influence on the diffusion kinetics, affecting the diffusion activation barrier by less than a few percent. The experimental results are in good agreement with density-functional theory calculations of Mattsson *et al.* (2003). These findings suggest that despite the fact that the tunneling parameters have some effect on the extracted diffusion and rotation barriers, they can often, at least to first order, be ignored. A second drawback is that, when an atom (or vacancy) diffuses to a neighboring site on the surface, the tracking tip quickly relocates to the atom's new position. However, in case that another atom or vacancy comes nearby the tip might be locked onto to this other atom. Such a relocking event cannot be discriminated from a regular diffusion event of the atom under study to a nearby position. The simplest way to check this is to record frequently normal STM images of the region in the proximity of the object under study.

As will be discussed in Sec. III.B not all conformational changes that are recorded with STM are thermally induced. Most of the tunneling electrons tunnel elastically; however, a small fraction of the electrons tunnel inelastically. The inelastic tunneling electrons can excite vibrational modes. These excitations can subsequently lead to bond breaking and bond formation (Hla *et al.*, 2000; Hahn and Ho, 2001, 2005; Kim *et al.*, 2002; Morgenstern and Rieder, 2002a, 2002b; Pascual *et al.*, 2003; Kumagai *et al.*, 2008, 2009), rotation, diffusion, molecular rearrangement and isomerization (Gaudioso *et al.*, 2000; Gaudioso and Ho, 2001a; Henzl *et al.*, 2006, 2007; Pitters and Wolkow, 2006; Pan *et al.*, 2009), and even to a change of chirality (Simic-Milosevic *et al.*, 2008, 2009; Parschau *et al.*, 2009). All these processes were examined with open feedback loop STM.

B. Open feedback loop scanning tunneling microscopy

The first open feedback loop experiments were performed by Lozano and Tringides (1995). They showed that the time dependence of the tunneling current can be used to extract information on the dynamic processes, such as surface diffusion, by measuring its power spectrum at different temperatures. Their procedure is rather straightforward; i.e., the fluctuations of the tunnel current are monitored with the tip held stationary over the surface in the open feedback loop configuration. The tunneling current is fed into a spectrum analyzer covering a frequency range from 0.02 to ~ 25 kHz. The high-frequency cutoff of ~ 25 kHz is set by the electronics. The measured power spectra were fitted to the expected theoretical ones corresponding to diffusive motion on the substrate. Although the extracted diffusion barrier was a little lower than expected, Lozano and Tringides, convincingly demonstrated that the dynamic range of STM can be significantly extended in the time domain.

As pointed out a small fraction of the electrons can tunnel inelastically and thereby excite vibrational, rotational, or translational modes of atoms or molecules that are imaged with the STM.

As an illustrative example we discuss an elegant experiment by the Ernst group (Parschau *et al.*, 2009). This group found that the adsorption of propene at 40 K on the intrinsically stepped Cu(211) surface results into two types of species of adsorbates, each occurring in two enantiomeric states (see Fig. 5). They were able to invert the enantiomeric state by inelastic electron tunneling. The conversion from state 2^* to state 1 requires a bias voltage of about 200 mV, which correlates with the C=C stretching mode at 204 meV, whereas the conversion from state 1 to state 2^* takes place at electron energies exceeding the symmetric CH_3 stretching mode at 360 meV. The conversion process can be monitored by positioning the tip over the molecule at fixed bias and measuring the current as a function of time in the open feedback loop configuration. A jump in the current indicates that a conversion of the molecule from one state to the other has occurred. Rescanning of the same area will reveal the nature of the transition. The flipping rate

FIG. 5. (Color online) Adsorption and dynamics of propene on Cu(211). (a) STM image ($6.1 \times 4.9 \text{ nm}^2$) recorded at 7 K of propene on Cu(211). The intrinsically stepped surface appears as dark and bright stripes. The bright stripes are located near the step edges. Two species of adsorbates (1,2) are observed both appearing in two mirror-related states (1, 1^* and 2, 2^* , respectively). (b) Lowest energy adsorption of states 1 and 1^* . (c) Lowest energy adsorption of states 2 and 2^* . From [Parschau et al., 2009](#).

for the enantiomeric conversion scales as the tunnel current to the power 2 indicating that two inelastically tunneling electrons are required for this process. Next we give a few more examples of these tunnel current-induced processes.

Stipe, Rezaei, and Ho used tunneling electrons from the STM tip to induce and monitor the reversible rotations of acetylene molecules on Cu(100) ([Stipe et al., 1998a](#)) and molecular oxygen on Pt(111) ([Stipe et al., 1998b](#)). The procedure they applied is as follows: the STM tip is placed accurately over a preselected molecule, a voltage pulse is given and subsequently the feedback is turned off, and the tunneling current is recorded. A rotation of the molecule will result in a change of the tunneling current. They illustrated that the number of equivalent orientations depends on the adsorbed molecule and the symmetry of the surface. For instance, acetylene molecules on a Cu(001) surface have two equivalent, but orthogonal, adsorption orientations, whereas the molecular oxygen molecules on Pt(111) have three equivalent adsorption orientations, which are separated by 120° . By monitoring the tunneling current above a single molecule one can easily obtain statistics of the residence times spent in the distinct orientations. Since the molecule has “no memory” of the time it has spent in any particular orientation, one will usually observe an exponential distribution of the residence times. The inverse of the exponential time constant gives the rotation rate, which depends on the tunneling current, the sample bias voltage, and the lateral position. Stipe,

Rezaei, and Ho proposed that the mechanism for single molecule rotation involves inelastic electron tunneling by means of an adsorbate-induced resonance. The maximum energy of the tunneling electrons is given by eV_b , where e is the magnitude of the electron charge and V_b is the bias voltage applied to the sample. In case that the energy of the electron is larger than the rotation barrier E_{rot} , the barrier can be overcome by one inelastic tunneling electron. In this single electron process the rotation rate scales linearly with the tunneling current I . For a maximum energy of the electrons that is smaller than the rotation barrier ($eV_b < E_{\text{rot}}$) we are dealing with a ladder-climbing mechanism: each inelastic tunneling electron promotes the molecule to a higher vibrational quantum state. Since the lifetimes in these higher excited states are usually very short, the rotation process is dominated by excitation processes that take the path with the smallest number of intermediate states that are energetically allowed. It follows that the overall rotation rate is proportional to I^n , with n equal to the number of electrons required to rotate the molecule. Hence the smaller the sample bias voltage, the higher n generally becomes.

In the case of acetylene on Cu(001) Stipe, Rezaei, and Ho showed that the rotational mode can be induced by excitation of the C—H stretch mode at 358 meV ([Stipe et al., 1998a](#)). They positioned the tip over the acetylene molecule [see Fig. 6(a)] and increased the sample bias voltage. At voltages that exceed the CH stretching mode (358 meV) sudden changes in the tunneling current were recorded [see Fig. 6(b)]. These changes in the tunneling current are due to a reversible change between the two equivalent adsorption configurations of acetylene on Cu(100). A histogram of the residence times in the two orientations exhibits an exponential distribution [shown for the high-current level in Fig. 6(c)]. By replacing hydrogen by deuterium the threshold energy dropped, as expected, to 266 meV (C—D stretch mode). In a subsequent paper ([Stipe et al., 1999](#)) they replaced only one of the hydrogen atoms by deuterium and studied the rotation of C_2HD on Cu(001). At 300 meV only the C—D mode and not the C—H mode can be excited. Due to the spatial localization of the inelastic tunneling the molecule rotates about ten times faster when the C—D bond is under the tip than when the C—H bond is under the tip. These rotation experiments were performed at low temperatures (8 K) where the rotation process is thermally hindered, however, at higher temperatures ($> 70 \text{ K}$) the rotation becomes thermally activated ([Stipe et al., 1999](#)). These landmark experiments as well as several others ([Gaudioso et al., 1999](#); [Gimzewski and Joachim, 1999](#); [Lauhon and Ho, 1999](#); [Gaudioso and Ho, 2001b](#)) revealed that STM cannot only be used to study the chemistry but STM is also capable of inducing and performing detailed studies of the dynamics of individual molecules.

Parallel and independent to the pioneering work of the Ho group, [Sato, Iwatsuki, and Tochiyama \(1999\)](#) and [Hata, Sainoo, and Shigekawa \(2001\)](#) performed time-

FIG. 6. (Color online) Adsorption and dynamics of acetylene on Cu(100). (a) Schematic of acetylene on Cu(100) showing side and top views of the molecular adsorption site and orientations consistent with the STM images. The dashed line represents the outline of the dumbbell-shaped depression in STM images. The asterisk refers to the position of the STM tip. The images are scanned at a tunneling current of 10 nA and a sample bias of 100 mV. The square lattice represents the position of the atoms of the Cu(100) surface. (b) Current during a 364 mV voltage pulse over an acetylene molecule initially in the high-current orientation, while the STM tip remains fixed 0.15 nm off center. Each jump in the current indicates the moment of rotation of the molecule. (c) Distribution of the times the molecule spent in the high-current orientation with a fit to an exponential decay with a time constant of 184 ms. From [Stipe *et al.*, 1998a](#).

resolved scanning tunneling microscopy experiments on the (001) surfaces of the group-IV semiconductors. Both groups recorded current time traces on the dynamic flip-flopping dimers of the bare substrates. As an example we discuss a series of open-loop STM experiments performed on the bare Ge(001) surface. In order to explain these experiments properly we have to discuss the (001) surfaces of the group-IV semiconductors. The silicon and germanium (001) surfaces are among the most frequently studied surfaces ([Zandvliet, 2000, 2003](#)). The unreconstructed Si and Ge(001) surfaces have two broken bonds (dangling bonds) per surface atom (see Fig. 7). This high density of dangling bonds per surface atom is from an energetic point of view unfavorable since the free energy per unit area of a surface scales with the number of broken bonds per surface atom. The (001) surfaces reconstruct by the formation of surface dimers. This dimerization leads to a reduction of the number of dangling bonds from two per surface atom in the unre-

FIG. 7. Ball and stick models of the silicon and germanium (001) surfaces: (a) 1×1 (unreconstructed) surface, (b) $p(2 \times 1)$ dimer reconstruction, (c) $c(4 \times 2)$ dimer reconstruction, and (d) $p(2 \times 2)$ dimer reconstruction. The surface unit cells are outlined.

constructed case to only one dangling bond per surface atom in the reconstructed, i.e., dimerized, case. Besides the short-range interaction that leads to dimerization, the (001) surfaces also exhibit a weaker long-range interaction that leads to various higher-order surface reconstructions, such as $p(2 \times 2)$ and $c(4 \times 2)$ (see Fig. 7).

In 1985 the first STM images of the Si(001) surface ([Tromp *et al.*, 1985](#); [Hamers *et al.*, 1986](#)) revealed that most of the surface dimers have a symmetric appearance. However, as has been well established since the late 1970s, the lowest energy configuration is a buckled dimer ([Chadi, 1979](#)), and the observed symmetric dimers are actually rapidly flip-flopping between the two possible buckled configurations. The first direct evidence for this flip-flop motion was provided by [Sato, Iwatsuki, and Tochihara \(1999\)](#). They demonstrated that the tunneling current recorded above one of the atoms of a dimer of the Ge(001) surface exhibited telegraphlike noise. Later similar experiments were reported for Si(001) by [Hata *et al.* \(2001\)](#), [Yoshida *et al.* \(2002\)](#), and [Pennec *et al.* \(2006\)](#). The latter measurements demonstrated that the flip-flop motion of the dimers can be interpreted in terms of a so-called phason. A phason is a phase defect or antiphase boundary in the dimer alignment (see Fig. 8). At an antiphase boundary one of the neighboring dimers is in the “right” orientation, whereas the other is in the “wrong” orientation. At sufficiently

FIG. 8. (Color online) Schematic diagram of a diffusing phason. The phason diffuses from a distance $3a$ from the origin in (a) to a distance $5a$ from the origin in (c). One diffusion “step” of a phason corresponds to a single flip-flop event of one of the constituting dimers of the phason.

FIG. 9. (Color online) Filled-state room-temperature STM image of Ge(001). The sample bias is -1.5 V and the tunneling current is 0.4 nA. The boundaries between the local $c(4 \times 2)$ and (2×1) reconstructions are indicated by white lines. The inset shows a schematic representation of a buckled dimer. The tilt angle of the dimer bond is 10° – 20° .

high temperatures these phasons perform a thermally activated random walk within the substrate dimer rows. If at an antiphase boundary one of the dimers flips to its other buckled configuration, the phason effectively moves by one lattice spacing (see Fig. 8). A dimer which is positioned under an STM tip will thus flip to its other buckled configuration each time that a phason traverses the tunnel junction. Such an event will lead to a jump in the tunneling resistance and thus to a sudden decrease in the tunneling current.

Figure 9 shows a room-temperature scanning tunneling microscopy image of the Ge(001) surface. The surface shows an ordered $c(4 \times 2)/(2 \times 1)$ domain pattern. The dimers in the (2×1) domain appear symmetrically, while the dimers in the $c(4 \times 2)$ domain appear asymmetrically. Within a single substrate dimer row the dimers buckle nearly always in an opposite registry, meaning that neighboring dimers buckle in opposite directions. The zigzag order partially relaxes the stress generated by the buckling of the dimers. In-phase buckling of adjacent dimer rows leads to a $p(2 \times 2)$ reconstruction, whereas out-of-phase buckling of adjacent dimer rows leads to a $c(4 \times 2)$ reconstruction (compare Fig. 7). In the two latter cases, it is generally believed that the asymmetric appearance of the dimers implies that the flip-flop motion is frozen in and that these dimers do not exhibit any flip-flop motion.

In Fig. 10(a) we show a filled state STM image of the Ge(001) surface wherein the flip-flop motion of the Ge dimers can be observed. Dimers that appear symmetrically are visible in the lower-left and upper-right corners of the image. In the middle of the image two missing dimer defects are visible (dotted white circles). The missing dimer defect on the left induces buckling of the nearby dimers, whereas the right one results in dimers that appear symmetrically. Both dimer rows that contain the missing dimer defects have a noisy appearance, in-

FIG. 10. (Color online) Dynamics of Ge dimers in the proximity of missing dimer defects. (a) Filled-state STM image of Ge(001). The sample bias is -1.5 V and the tunneling current is 0.4 nA. The dimers appear fuzzy in some of the substrate dimer rows. This flickering is a result of the flip-flop motion of the dimers during imaging. The flickering is most pronounced in dimer rows that contain missing dimer defects. Note that this flickering occurs in a symmetric dimer row (right defect) as well as in an asymmetric dimer row (left defect). Labels 1–4 refer to the different types of dimers [a flickering asymmetric dimer (1), a flickering symmetric dimer (2), a nonflickering symmetric dimer (3), and a nonflickering asymmetric dimer (4)] over which the tunneling current is measured as a function of time. (b) Some of the dimer positions where the current is measured as a function of time are labeled A–F. Note that (b) is rotated with respect to (a).

dicative of a rapid flip-flopping motion of the dimers. Interestingly, the flickering is not only observed in the dimer row that appears symmetrically but also in the one that appears asymmetrically. This observation conflicts directly with the traditional picture of static (i.e., not flip-flopping) buckled dimers in the $c(4 \times 2)$ domains. It should be mentioned that there are also buckled dimers that do not exhibit any flip-flop motion at least not on the time scale that is accessible to the instrument. Their motion is either too slow or too fast for to be observed.

The flip-flop motion of the dimers is a consequence of the presence of phase defects (phasons) in the dimer alignment. The dimer under the tip is flipped each time a phason makes an in-plane traversal of the tip-surface junction. To investigate the dynamics of the dimer flip-flop motion in more detail, the tunneling current is measured over each pixel of Fig. 10(a). Some of the dimer positions where the tunneling current is measured as a function of time are labeled A–F in Fig. 10(b).

Figure 11 shows a typical current trace measured above a flickering asymmetric dimer [curve (1)], above a flickering symmetric dimer [curve (2)], above a nonflickering symmetric dimer [curve (3)], and above a nonflickering asymmetric dimer [curve (4)]. The arrows in Fig. 10(a) mark the positions where these current traces are recorded. From the telegraph noise it can be clearly seen that the flickering asymmetric dimer has a preference for one of the two buckled states, whereas the flickering symmetric dimer does not exhibit such a preference. It is

FIG. 11. (Color online) Current traces measured on the dimers of a Ge(001) surface. The current is recorded over a flickering asymmetric dimer [curve (1)], a flickering symmetric dimer [curve (2)], a nonflickering symmetric dimer [curve (3)], and a nonflickering asymmetric dimer [curve (4)]. The sampling rate is 50 kHz. Current set points are 0.40 nA for traces (1)–(3) and 0.55 nA for trace (4).

most likely that the flip-flop frequency of the nonflickering symmetric and asymmetric dimers is so high that it lies outside the bandwidth of the STM preamplifier (≈ 50 kHz).

The distribution of the residence times of the dimers in each of the two buckled states is shown in a histogram $P(t)$ for the flickering symmetric dimers in Fig. 12 and for some of the flickering asymmetric dimers in Figs. 10(b) and 13(a)–13(d). Assuming that the flip-flop motion is a random process, the theoretical lines are obtained from

$$P(t) = \frac{N}{2} p_{ij} (1 - p_{ij})^t, \quad (1)$$

where p_{ij} is the probability to flip from state i to state j , N is the number of flip-flop events, and t is the time. The factor $N/2$ appears because half of the flip-flop events are from state i to state j and the other half from state j to state i . N and p_{ij} are determined from the distribution of the residence times. All histograms of the measured residence times in Figs. 12 and 13(a)–13(d) exhibit Poisson behavior. The average residence times in the two

FIG. 12. (Color online) Histogram of the residence times in the two buckled states of a symmetric appearing flickering dimer from Fig. 10(a). The gray line is the theoretical fit for a random process (the Poisson distribution). $\tau(1)$ and $\tau(2)$ are the counts for the residence times in the two buckled states.

FIG. 13. (Color online) Statistics of the dynamics of dimers of Ge(001). (a)–(d) Histograms of the residence times for dimers A–D from Fig. 10(b). The lines are the corresponding theoretical curves for a random process. $\tau(1)$ and $\tau(2)$ are the counts for the residence times in each of the two buckled states.

configurations of the symmetric dimer are about the same, whereas they are significantly different for the dimers that appear asymmetrically. As a function of distance from the defect, via dimers A–F, the dimers show an alternating preference for either state (1) (dimers A, C, E, etc.) or state (2) (dimers B, D, F, etc.), in accordance with the observed $c(4 \times 2)$ (zigzag) reconstruction. [State (1) here means a dimer that is buckled such that the “left” atom of the dimer in Fig. 10(a) is higher: state (2) means that the “right” atom is higher.] The flipping frequency (extracted from the time-resolved measurements) gradually increases as a function of distance from the defect. A detailed study of the spatial variation on the flip-flop frequency in the proximity of surface defects revealed that the interaction of the phasons with the long-ranged strain fields can explain the observations well (van Houselt *et al.*, 2006). The difference in average residence times in the two buckled states of the dimers that appear asymmetrically allows us to determine the energy difference of the two buckled configurations (van Houselt *et al.*, 2006). Phasons are not always mobile as illustrated for the Au/Ge(001) system where the dimer at the location of the antiphase boundary continuously flips back and forth between its two buckled states (van Houselt *et al.*, 2008). What is, however, the exact reason of the pinning of the phasons for the Au/Ge(001) remains a mystery so far.

During the past decade many examples of thermally induced or tunneling current-induced conformational changes have been observed, such as the rotation of *cis*-2-butene on Pd(110) (Sainoo *et al.*, 2003, 2005), the rotation of the zinc-octaethylporphyrin molecule incorporated in the holes of a network generated by the thermal dehydrogenation of 4,9-diaminoperylenequinone-3,10-diimine on a Cu(111) surface (Wahl *et al.*, 2007), the switching of *N*-(2-mercaptoethyl)-4-phenylazobenzamide on Au(111)

(Yasuda *et al.*, 2003), the bistability of biphenyl molecules or 1,5 cyclo-octadiene on Si(001) (Lastapis *et al.*, 2005, 2008; Martin *et al.*, 2006; Nacci *et al.*, 2008a, 2008b), and the hydrogen automerization of naphthalocyanine on a NaCl bilayer on Cu(111) (Liljeroth *et al.*, 2007).

The open feedback loop STM technique has also been successfully applied to study related physical phenomena such as quantum tunneling of Sn adatoms at the Sn/Ge(111) surface (Ronci *et al.*, 2005, 2006, 2007), adsorption of hydrogen on Ge(001) (Saedi, Poelsema, and Zandvliet, 2009), the electronic switching of silicon adatoms by molecular-field effects on Si(111) (Harikumar *et al.*, 2006), diffusion of Cu and Ag on Si(111) (Wang *et al.*, 2005, 2008), switching of Co atom between hcp and fcc sites on Cu(111) (Moore *et al.*, 2007), conductance switching of single oligo(phenylene ethynylene) molecules (Stroscio and Celotta, 2004; Stroscio *et al.*, 2006), the transport through a single octanethiol molecule (Kockmann *et al.*, 2009), and even the current-induced magnetization switching of iron nanoislands on W(110) (Krause *et al.*, 2007).

IV. DYNAMICS OF NANOSCALE MOLECULAR ASSEMBLIES

The concept of a “machine”—a mechanical or electrical device that transmits or modifies energy to perform a certain task—can be extended to the nanoworld. On the nanoscale, the nanomachine components would be small atomic or molecular assemblies each designed to perform a specific task which, all together, would result in a complex function. In general these nanomachines cannot be built by further miniaturizing machine blueprints from the macroworld.

STM and, in particular, time-resolved STM, is a powerful technique to study nanomachines, such as rotors and simple motors, on surfaces. Molecular motors are of indispensable value for life since they perform tasks such as organizing the cellular cytoplasm by vesicle transport, powering of the motion cells, and body movement through muscle contraction. Since the late 1980s several systems that exhibit thermally induced molecular rotation have been reported (Alvey *et al.*, 1987; Mo, 1993; Gimzewski *et al.*, 1998; Stipe *et al.*, 1998b; Rao *et al.*, 2003). The rotation of porphyrins has been studied quite extensively with STM (Hersam *et al.*, 2000; Stöhr *et al.*, 2001; Rao *et al.*, 2004; Iancu and Hla, 2006; Vaughan *et al.*, 2006; Ye *et al.*, 2006; Wintjes *et al.*, 2007). Other appealing systems are thioethers (Baber *et al.*, 2008) and tetra-*tert*-butyl zinc phthalocyanine (Gao *et al.*, 2008) on Au surfaces.

In a recent STM study Baber, Tierney, and Sykes (2008) showed that thioethers of various lengths are simple and robust rotors that can be actuated both thermally and mechanically. The rotation can be switched on and off reversibly by dragging the molecules with the STM tip toward or away from one another. Isolated dimethyl, diethyl, dibutyl, and dihexyl sulfides start to exhibit thermally induced rotation at temperatures of <7, 17, 15, and 17 K, respectively (see Fig. 14). Macroscopi-

FIG. 14. (Color online) STM images revealing thermal activation of thioether rotors on Au(111): dimethyl, diethyl, and dihexyl sulfide. The temperatures in the right column are the onset temperatures for the rotation process. The sample bias was -300 mV and the tunneling current was 9 pA. From Baber *et al.*, 2008.

cally one would expect that the longer and heavier the molecules, the more thermal energy it requires to start rotating. From the quantum-mechanical point of view, however, a rotor with a larger moment of inertia is easier to excite than a small rotor. Baber, Tierney, and Sykes showed that neither the classical nor the quantum-mechanical picture for the rigid rotor accurately describes the behavior of the thioether rotor system properly. Current time traces (see Fig. 15) recorded at various temperatures for dibutyl sulfide revealed another intriguing result, namely, an anomalous low attempt frequency of only $\sim 7 \times 10^7$ Hz. This suggests that the rotation process is a multistep process. The latter is probably due to the fact that both arms of the rotor have to overcome the torsional barrier simultaneously and in phase with one another.

We have only focused our attention so far on the dynamics of individual atoms or molecules. In a recent study by Saedi, van Houselt, *et al.* (2009) the dynamics of a dimer pair was studied using open feedback loop current time traces. Figures 16(a) and 16(b) show STM images of the studied dimer pairs. Saedi, van Houselt, *et al.* (2009) showed that the two dimers can be brought into motion independently by careful positioning the tip in the proximity of the dimer pair [see the STM images in Figs. 16(c) and 16(d)]. Although the flipping process is a stochastic process, its average value can be tuned accurately by the tunnel current. Figure 17(a) shows the linear relationship between the measured flip-flop frequency of the dimer pairs and the tunneling current,

FIG. 15. (Color online) Tunneling current vs the time recorded over a dibutyl sulfide molecule on a Au(111) surface. Sudden jumps in the current indicate changes in the position of the alkyl tail of the thioether with respect to the STM tip. Three current levels correspond to the three inequivalent orientations of the dibutyl sulfide molecule with respect to the position of the STM tip (indicated by the black dot). From [Baber *et al.*, 2008](#).

which indicates that the dimer-pair motion is a single electron process. Moreover, a linear extrapolation of the relation between the frequency and tunnel current reveals that the curve intersects the origin of the graph.

FIG. 16. (Color online) Dynamics of Pt atomic chains on Ge(001). (a) An STM topograph of atomic chains on Ge(001) at 4.7 K. Image size is $65 \times 65 \text{ \AA}^2$, bias voltage is -1.5 V , and tunneling current is 0.5 nA . The atomic chains show up as bright protrusions running from the bottom to the top in the image. (b) Top view of a regular dimer pair at 77 K, bias voltage of -1.0 V , and tunneling current of 0.8 nA . The atomic chain runs from left to right in this image. (c) and (d) Two subsequent images of a dimer pair that exhibits dynamics. The atomic chains run from left to right in these images. The reconfiguration of the dimer pair takes place on a time scale which is far below the time needed to conduct one STM image and shows up as a discontinuity as the tip is scanned across the chain. (Note that the fast scanning direction is from top to bottom, the slow scanning direction is from left to right in this images.)

FIG. 17. (Color online) Statistics of the dynamics of Pt atomic chains on Ge(001). (a) The measured flip-flop frequency of the dimer pair as a function of the tunneling current. The frequency depends linearly on the tunnel current and passes through the origin (see the least-squares fit indicated by the dotted line). Each data point plotted is the average of 100 values. (b) Current traces, showing telegraphic signals, resulting from different dimer-pair flipping modes at 77 K (measured with open feedback loop, bias voltage of -1.0 V , and set-point current of 1.0 nA). The graph is corrected for slow variations in the tunnel current as a result from drift of the STM tip. The dimer pair switches between six well-defined states, indicated by the dotted lines in the graph.

This implies that the motion of the dimers is exclusively current induced. In Fig. 17(b) an example of a current time trace recorded on a dynamic dimer pair is shown. In this particular case the system exhibits six different current levels in a time window of 82 s. Saedi *et al.* found also time traces with two, three, or four current levels (see Fig. 18). It should be mentioned here that all current time traces in Figs. 17 and 18 are recorded at 77 K.

In Fig. 18(a) a simple two-level current time trace is depicted. The current flips back and forth between a low and a high level. Due to the fact that the tip slightly drifts away from the surface the current decays. Figure 18(a) shows that the average flipping frequency decreases with decreasing current. Figure 18(b) shows three current levels, whereas Figs. 18(c) and 18(d) show four different current levels. All these traces can easily be understood in terms of a simple model where both dimers can “flip” independently. In Fig. 19(a) the boundary positions of a flipping dimer pair are shown as extracted from many STM images. The motion of the flipping dimer pair resembles an atomic pinball machine. Figures 19(b) and 19(d) show the different possibilities for the motion of the flipping dimer pair. Figure 19(c) shows schematically the corresponding current levels. In one of the observed flipping modes [flipping mode 6; Fig. 19(d)] the dimers flip in phase. The closely related out-of-phase flipping mode (flipping 5) has, however, never been observed experimentally.

V. CONCLUSIONS

The strength of STM to directly visualize surfaces and surface processes down to the atomic scale cannot be overestimated. It is not surprising that the ability to see things in many cases removes doubts and uncertainties regarding the system under study. Despite this appealing high spatial resolution the STM technique also suffers

FIG. 18. (Color online) $I(t)$ measurements of the dynamic dimer pair at 77 K with open feedback loop and a bias voltage of -1.0 V. The set points of the tunnel current are (a) 1.5, (b) 0.8, (c) 0.8, and (d) 1.5 nA. The dynamic dimer pair flips back and forth between two well-defined current levels. The decrease of the tunnel current with time in (a) results from the drift of the STM tip. Panels (b)–(d) are corrected for this drift. (b) Three well-defined current levels, of which one is common in both observed flipping modes. (c) and (d) Four current levels, with two different transitions between the two flipping modes. The different flipping modes are shown in Fig. 19(b).

from a number of disadvantages. One disadvantage is the rather poor temporal resolution. Recent developments in the field have, however, led to a significant improvement of this time resolution. The STM can in principle be modified in such a way that images can be recorded with frame rates of less than 1 s. But even without modifying the microscope, which is a formidable task in itself, well-tailored and properly designed open-loop and closed-loop measurements allow time resolutions as low as 10–100 μ s. In order to further improve the time resolution, STM preamplifiers with higher bandwidths should be developed. The available although still limited number of published papers in this particular field have revealed an exciting view on the dynamic behavior of single atoms, molecules, and assemblies of molecules. Currently, the vast majority of these papers have focused on rather local processes and

FIG. 19. (Color online) Schematic overview of the various configurations of the flipping dimer pair. (a) Measured boundary positions of a flipping dimer pair extracted from STM topographs. The atoms of the dimer pair are marked as pivot atoms (p) or revolving atoms (r). The motion of the dimers is indicated by the gray arrows. The thick dashed lines indicate a down-down, down-up, or a up-up configuration. The motion of the dimer pair resembles the flippers of an atomic pinball machine. (b) Schematic of the flipping dimer pair. Each flipper is in either a down or an up configuration, resulting in four possible configurations. The pivot and revolving atoms are shown. Colors refer to the flipping modes highlighted in (a). The tip position is indicated with the triangle. (c) The four possible configurations in (b) can lead to six different flipping modes. (In mode 1, for instance, the first dimer flips up and down, while the second dimer remains in the up configuration.) Flipping mode 5 has never been observed experimentally. (d) Including an attractive interaction between the two revolving atoms of the flipping dimer pair leads to a smaller amplitude of oscillation as compared to the case where only one of the two flippers flips up and down. This shows up as an additional flipping mode with two corresponding additional current levels [dotted lines in (c)].

on small objects. The time-resolved STM approach is also applicable to more complicated and collective processes, such as surface phase transitions, mass transport, and domain wall fluctuations. One should, however, realize that the enhanced time resolution of the STM data goes at the expense of the available spatial information of the surface process under study. We envisage that a smart design of the measurement scheme, where standard STM imaging and open feedback loop current time traces are collected sequentially, may pave the way to the study of these complex systems. Although the majority of the studies that have been performed so far have focused on well-defined surfaces under nearly ideal conditions (low temperatures and ultrahigh vacuum), we anticipate that in the near future this technique will also be applied in other areas, such as biology, molecular electronics, and soft condensed matter. We are con-

vinced that the unique spatial resolution of the STM combined with the significantly enhanced temporal resolution will lead to many more new and exciting discoveries, which are not anticipated at present.

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