Field-based scanning tunneling microscope manipulation of antimony dimers on Si(001)

Please check the document version of this publication:

• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

Field-based scanning tunneling microscope manipulation of antimony dimers on Si(001)

S. Rogge,[a] R. H. Timmerman, P. M. L. O. Scholte, and L. J. Geerligs
*Department of Applied Physics and DIMES, Deft University of Technology, Lorentzweg 1,
2628 CJ Delft, The Netherlands*

H. W. M. Salemink
IBM Research Division, Zurich Research Laboratory, 8803 Ruschlikon, Switzerland

The manipulation of antimony dimers, Sb_2, on the silicon (001) surface by means of a scanning tunneling microscope (STM) has been experimentally investigated. Directed hopping of the Sb_2 dimers due the STM tip can dominate over the thermal motion at temperatures between 300 and 500 K. Statistics on the enhanced hopping are reported and possible tip–adsorbate models are discussed focusing on a field-based interaction. The low yield of directed hopping is believed to be due to the low gradient in the interaction energy intrinsic to a field-based mechanism. Ultimate resolution and limiting factors of this manipulation technique are discussed. © *2001 American Vacuum Society.*
[DOI: 10.1116/1.1372925]

I. INTRODUCTION

In recent years the scanning tunneling microscope (STM) has been developed into a tool which can be used for observational as well as structuring tasks on the atomic scale. Clusters[1] and molecules[2] consisting of many atoms (60–1000) have been manipulated on semiconductors at room temperature. Manipulation with control down to single atoms is still limited to adsorbates on metals at low temperature[3] except for etching techniques down to the breaking of individual bonds.[4,5]

Due to the growing interest in the electronic structure of nanometer sized conductors we have investigated the possibility of creating arbitrarily shaped structures approaching the atomic scale on a semiconductor. There are not many studies focusing on the manipulation of adatoms on semiconductors. Pioneering work by Whitman *et al.*[6] showed that the large electric field of a STM tip can induce motion of metal atoms on a semiconductor surface [cesium on InSb and GaAs(110)]. They applied voltage pulses to the tip of the STM and observed increased coverage of Cs in the region below the tip (150–350 nm scan field), on a typical length scale of 50 nm. A model which assigns a permanent and induced dipole to the adsorbed Cs was proposed and the forces due to the tip field were analyzed leading to acceptable agreement.

Both Whitman *et al.* and Mo[7] proposed a model based on effectively lowering the diffusion barrier by the tip–adsorbate interaction. Mo demonstrated an increase in the diffusion rate of antimony dimers, Sb_2, on Si(001) due to STM scans. The large field of the tip induces a dipole in the adsorbate and the energy change associated, $W_{tip} = -\mathbf{p}(\mathbf{E}) \cdot \mathbf{E} = -\alpha E^2$, can be as large as 1 eV considering a field of $E = 10$ V/nm and the polarizability of a free Sb atom $\alpha = 1.1 \times 10^{-39}$ C m²/V.[8]

Directed manipulation of single adsorbates, in contrast to undirected enhancement of diffusion, has only been achieved for tip–adsorbate interactions which are shorter ranged than the long range forces due to the electric field of the tip, and for much smaller surface diffusion barriers. In particular low temperature manipulation of ad-atoms and clusters on metals was achieved by short-range attractive and repulsive forces probably based on a van der Waals potential.[3,9] Repulsion between the tip and adsorbate was also used in the case of clusters and molecules[1,2] at room temperature. The possibility of using a field-based interaction to achieve atomic scale manipulation will be investigated.

In this article, we study the directed manipulation of Sb_2 ad-dimers on Si(001) and investigate a model based on a force between the adsorbate and the tip due to the gradient of the electric field. If the anisotropy in the motion resulting from the tip field is sufficiently large Sb_2 ad-dimers can be moved to any one of the possible grid positions on the substrate.

Antimony on Si(001) is an interesting subject since Sb is a silicon dopant. After overgrowth or even as surface atoms Sb patterns may have continuous electronic states. Futhermore, Sb_2 diffusion on Si(001) has been studied in detail previously. The dimers do not move at room temperature on the Si(001) surface on the time scale of the experiment (hours). A temperature increase to 400 K will already introduce many Sb_2 hops during one STM scan.

Data on Sb_2 dimer movement on the Si substrate will be shown for different manipulation parameters. All manipulation attempts are done with the feedback loop active by changing the gap bias voltage in a range of 1–5 V, set-point current $I_0 = 0.1$–25 nA, scan speed 10 nm/s–2 μm, and at low as well as high feedback gain. Besides hopping statistics of many dimers in a large scan field, manipulation of single dimers has also been investigated.

The energy change for moving a dimer with a permanent dipole changes sign resulting in an attractive and repulsive region, depending on tip–adsorbate distance on the surface. The energy scales in the case of a permanent dipole are smaller than for an induced dipole in Sb_2 on Si(001). There-

---
[a]Electronc mail: s.rogge@tnw.tudelft.nl

fore, a permanent dipole is less likely related to the observed behavior. The yield of the manipulation (directed movement) is low but we were able to manipulate a single Sb_2 dimer on the surface with a tunneling gap >0.5 nm. By analyzing the force on an adsorbate we will show that the relative change in energy for moving an induced Sb_2 dipole on the surface toward the tip is considerably smaller than the $0.5-1$ eV proposed earlier.[7] However, the resulting change in energy (on the order of the thermal energy) is consistent with the observed increase in Sb_2 hopping rate.

II. SAMPLE PREPARATION

For most of the experiments we use *p*-type Si(001) wafers (0.2 Ω cm). The oxide protected substrate is degassed in an ultrahigh vacuum (UHV) system with a base pressure below 5×10^{-11} mbar and flashed to 1500 K for several seconds. The sample is cooled from 1100 K to room temperature at a rate of approximately 1 K/s. We use a commercial variable temperature STM. The samples are heated by passing a direct current through the Si. This heating method is used for the surface preparation, as well as for scans in the STM at elevated temperature. Above 500 K Sb exhibits epitaxial 1×2 growth on the 2×1 Si(001) surface.[10]

The Sb is deposited from an *e*-beam evaporator and the coverages have been determined from the STM observations. The quoted temperatures are measured with a pyrometer and extrapolated below 750 K based on the heating current. The extrapolation of the temperature versus heating current introduces an appreciable error for temperatures below 500 K. We reproduced the thermal hopping rate of the Sb_2 dimers (at ''noninvasive'' scanning parameters, explained later) as a criterion to reproduce the temperature settings.

Electrochemically etched tungsten tips are used for the STM. The tips are degassed by electron bombardment after loading into the UHV. Further cleaning and sharpening is achieved by self-sputtering in neon as discussed in Ref. 11.

III. ANTIMONY ON Si(001)

Antimony evaporated from a source below 700 K onto a room temperature Si surface deposits mainly as Sb_4 clusters, which can be converted into Sb_2 dimers by annealing the system at 460 K for several minutes. If the surface is further annealed at 575 K the antimony self-assembles into short epitaxial lines.[10]

Antimony diffuses preferentially orthogonal to the dimer rows of the 2×1 Si reconstruction with a diffusion barrier of 1.2 eV. The diffusion rate parallel to the Si dimer rows is approximately 100 times lower.[7] The Sb_2 dimers are observed to be immobile at room temperature but they start hopping across Si dimer rows (as can be observed with the STM) at temperatures as low as 400 K.

Scans done at large voltages with the STM enhance the break up of the Sb_4 clusters as well as induce hopping of Sb_2 dimers to an adjacent Si dimer row[12,13] already at room temperature.
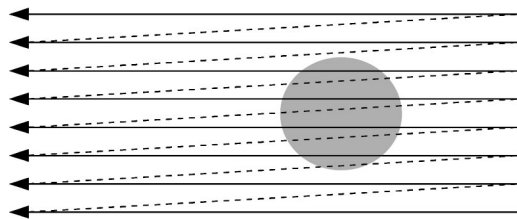
FIG. 1. Asymmetric tip scan. To manipulate the adsorbates on the surface the tip is scanned with ''invasive'' parameters (e.g., 5 V 0.3 nA) in one direction and then returned with the feedback settings of the gap used for observations (e.g., 1.5 V 0.1 nA).

IV. MANIPULATION

The scanning of a STM can enhance the hopping of a Sb_2 dimer on Si(001) to a neighboring dimer row. To achieve manipulation it is necessary to create a preferential direction in this additional motion of the Sb_2 dimer.

We have employed an asymmetric scan of the STM tip over the substrate trying to break the symmetry. In this technique we use parameters for the feedback loop of the tunneling gap which are different for scanning in the left-to-right direction compared to the right-to-left direction, as illustrated in Fig. 1. One of these parameter sets should be invasive, i.e., move the dimer, while the other should interact as little as possible (be noninvasive), allowing a net movement of the adsorbate.

Adjustable parameters for the manipulation of an adsorbate are: the tunneling current (I_0), bias voltage, the gain of the feedback loop, as well as the scan speed. The hopping rate of an adsorbate from one bonding site to the neighboring one can be tuned by changing the temperature of the substrate, resulting in a different distribution of energies within the potential well of the adsorbate in the surface corrugation. Tuning of the energy associated with the tip–adsorbate interaction compared to the confinement of the adsorbate on the surface should make it possible to find a parameter set, which allows the manipulation of the Sb_2 dimer. This, and the introduction of an asymmetry, will be discussed in detail below.

Figure 2 shows three subsequent scans at 500 K in which we have used asymmetric scan parameters. The surface was annealed at 575 K and therefore some epitaxial antimony lines have formed. The small bars in the image indicate which of the antimony dimers moved between subsequent

FIG. 2. Asymmetric scan of Sb on Si(001). These three scans where taken subsequently at 500 K after annealing the sample at 575 K. The tip is scanned at -2 V$_{substrate}$ and 0.1 nA from left to right and then returned at -5 V$_{substrate}$ and 0.3 nA from right to left. The bars indicate the position of a dimer which moved in the following frame. Here we find net movement of the free dimers along the tip sweep at high field.
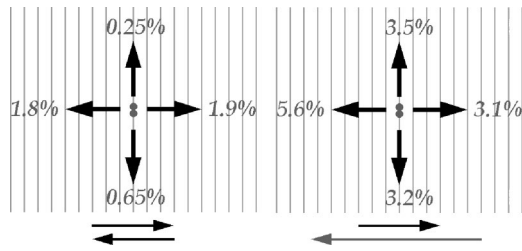
FIG. 3. Schematic shows the hopping rates for an observational (left) and an invasive (right) scan at 500 K. The lines indicate the direction of the substrate dimer rows which run parallel to the Sb dimer. The percentages indicate the relative number of dimers which moved in a certain direction during a scan (typically 80–120 dimers in the scan field, averaged over many scans). The noninvasive scan was done at -1.5 V 0.1 nA; the invasive one at rightwards -1.5 V 0.1 nA and leftwards -1.5 V 2 nA 0.05% loop gain.
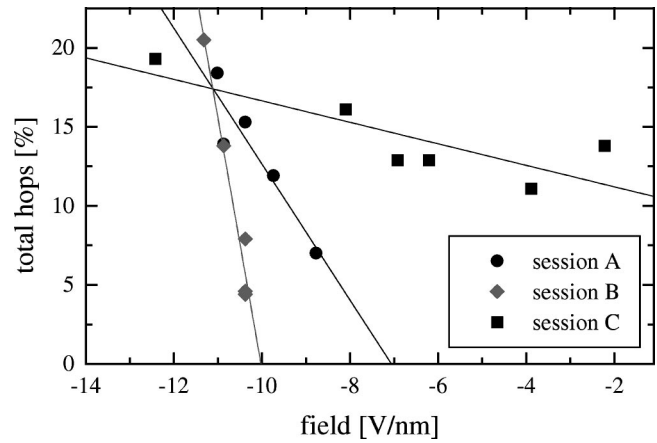

FIG. 4. Tip induced motion. The percentage of total hops is the sum of hopping events in any direction divided by the total number of dimers in the scan range $\times 100\%$. The quantity is plotted vs tip field for three different scan sessions of the same sample and tip resulting in three different slopes. This shows that the tip induced hopping does not simply depend on the field. We suggest that different tip terminations change the gradient of the field resulting in a scaling of the slopes.

scans. In these scans we observe a net movement of dimers toward the left, the same direction as the tip scan with ''invasive'' parameters (see the figure caption for details). In all experiments (series of consecutive scans at elevated temperature) we exclusively observed free dimers moving, in contrast to Sb_4 clusters or dimers, polymerized into an epitaxial line.

From many experiments as in Fig. 2 statistics have been established by averaging over many frames (with in total about 100 dimers/frame) and analyzing the deviation from the mean numbers of hopping dimers in the single scans of the series. The schematic in Fig. 3 illustrates the percentage of dimers hopping in a certain direction referenced to the total number of dimers in a scan area. The error bars are approximately one tenth of the quoted percentage. These statistics were obtained at 500 K for a noninvasive scan from left-to-right (-1.5 V 0.1 nA fast feedback) and for an invasive scan in the right-to-left direction (1.5 V 2 nA slow feedback, $5I_{set}$ current overshoot at the dimer). Due to poor tip stability at positive substrate bias we do not have sufficient data to discuss a field direction effect since most of the statistics were obtained with negative bias. However, in the few runs with positive substrate bias we observed qualitatively the same behavior as with negative bias. The left panel, of the noninvasive scan, shows clearly that the preferential diffusion direction of the Sb_2 dimers is indeed orthogonal to the dimer row. The right panel illustrates the mean movement during asymmetric sweeps with the parameters mentioned (error approximately one-tenth of the quoted percentages). We observed the preferential direction of motion now to be along with the invasive tip movement (this can be reversed as discussed below). Motion along the dimer rows has been enhanced; it is as pronounced as the motion against the invasive scan direction.

Figure 4 shows the total number of dimers hopping at various tip fields for different scanning sessions. In this case we used symmetric scans with identical parameters in both directions. The field quoted is defined as the bias voltage divided by the tip–surface distance resulting in an upper limit of the actual field. The absolute tip–surface distance was estimated by fits of the current versus relative tip height measurements for the voltages used. The three curves were

taken for an identical sample with the same tip on different days with fresh surface preparation each time. All controllable parameters remained the same yet the onset of hopping is substantially different.

The relative net-hopping rate for a large number of experiments is shown in Fig. 5 where a positive value denotes the fraction of dimers moving in the same direction as the invasive scan, $\Delta = (N_{left} - N_{right})/(N_{left} + N_{right})$. The error bar for these numbers is at most 10% determined in the same way as mentioned in the context of Fig. 3. It is important to note that each data point outside $\pm 10\%$ corresponds to a series of scans which all had a significant net movement of dimers in one direction.

Slow feedback (low loop gain) as well as high scan speed can be used to create an additional increase in the field close
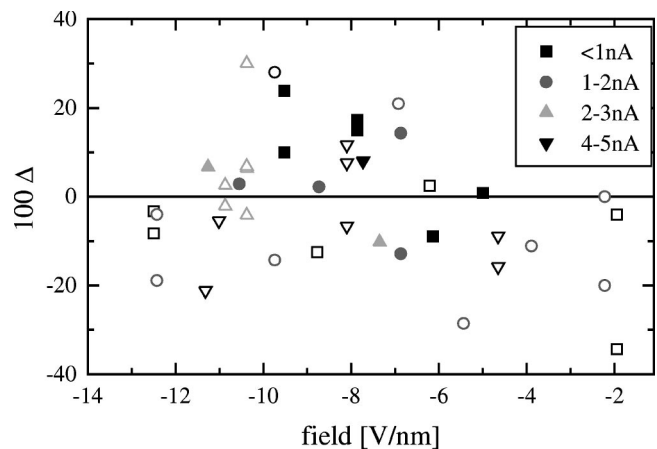

FIG. 5. Net hopping direction. The graph shows the relative motion of Sb_2, $\Delta = (N_{left} - N_{right})/(N_{left} + N_{right})$, for various tip fields. The symbols denote ranges of the tunnel current used during the invasive scans (right to left) and so a positive Δ denotes motion along with the invasive sweep. Open symbols indicate low loop-gain scans. The data were not all taken with the same sample and tip but all controllable parameters were kept constant.
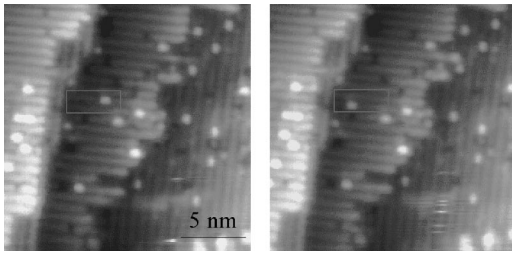
FIG. 6. Single dimer manipulation. The left STM scan shows Sb_2 dimers on several Si(001) terraces. An asymmetric tip scan was employed in the box over one dimer. The leftward sweep was at -5 V 0.2 nA and the rightward sweep identical to the observation parameters of -1.5 V 0.1 nA. After ten lines of this sweep the surface is rescanned. The dimer moved toward the step edge along the direction of the invasive scan and one dimer row (its preferential direction). The neighboring dimers did not move. This scan was done at 500 K where some diffusion occurs. The experiment demonstrates that the field is local enough to manipulate a single dimer.

FIG. 7. Cylindrical components of the field of a spherical tip. charge. The dashed curve represent the field normal to the substrate and the solid curve the in-plane component both as a function of in-plane distance, r, to the tip ($R_{tip}=5$ nm, $h_{tip-sample}=1$ nm, $V_{bias}=3$ V, $d_{depletion}=10$ nm). The in-plane term shows a maximum in magnitude which is not directly under the tip.

to the dimer. In the low loop-gain experiments the peak current was used to determine the field listed in Fig. 5 (open symbols). The tip does not make contact with the dimer (verified by the current trace during the manipulation), hence this technique is also long range.

A remarkable observation is that the induced motion of the Sb_2 dimers can be along with as well as against the direction of the invasive scan. There is no obvious trend with respect to the applied field (bias/height). However, the average of the low loop-gain experiments (higher current "before" the tip passes the center of the Sb_2 dimer) shows a tendency for hopping toward the tip, open symbols in Fig. 5. We think that a low loop gain breaks the symmetry of the tip–adsorbate system by creating a larger field when the tip first encounters the ad-dimer compared to when it has passed over it. This will be discussed in more detail in Sec. V in the context of the tip/adsorbate interaction model.

We have investigated the possibility of manipulating a single dimer, by using an asymmetric sweep with invasive parameters solely over only one ad-dimer and an noninvasive scan in the larger scan field for observation. As shown in Fig. 6 the field is localized enough even at the invasive parameters used (-5 V, 0.2 nA) to move the single ad-dimer. Affecting only one dimer is quite reproducible but the yield of these manipulations is not very high. This is consistent with the small fraction of dimers hopping (a few out of 100) in full scans as indicated by the percentages in Fig. 3. We present no quantitative yield for the single dimer manipulation since we do not have enough events for accurate statistics.

Going to higher fields was marginally possible in experiments on single dimers (not for the statistical approach based on many asymmetric scans). High fields (large tunneling current at a high gap voltage, e.g., >3 nA, 5 V) very frequently result in a severe change of the tip geometry or field evaporation of Si. In these experiments we did not observe a high yield of directed manipulation.
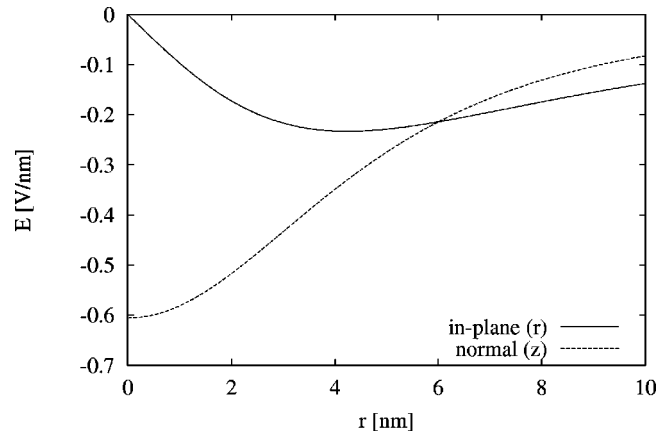
V. TIP–ADSORBATE INTERACTION

An "impact"-based mechanism seems unlikely for Sb_2 since the dimer appears in the STM to be only approximately 0.13 nm high. The currents required for stabilizing the tip at this separation are enormous and would destroy tip and/or substrate on the nanometer scale. Therefore we did not implement this technique. The low loop-gain experiments mentioned above still showed a finite maximum current (<20 nA) close to the dimer, hence no contact was made. Transfer of a Sb_2 dimer from the surface to the tip was not observed in any of our experiments (no missing dimers in large series of consecutive scans) unless the surface was destroyed.

We will discuss a model for the observed behavior based on the force due to the electric field of the STM tip. The tip–adsorbate interaction can be modeled by a dipole in the field of a point charge. A spherical tip of radius R can be represented as a point charge of such a magnitude to have an equipotential sphere of radius R at the potential of the bias voltage. This radius R is thus approximately the radius of curvature of the actual tip. Zero potential is defined at a depth in the silicon comparable to the size of the depletion layer. The components normal and parallel to the surface of such a field are plotted in Fig. 7.

The adsorbate is modeled as an isotropic linearly polarizable dipole $\mathbf{p}(\mathbf{E})=\alpha\mathbf{E}$, where α is the polarizability. The energy W of an induced dipole in the field E of a point charge is $W=\mathbf{p}\cdot\mathbf{E}$. This can be written as a function of the in-plane distance (r) to the point below the tip:

$$W(r,z)=-\alpha\left(\frac{V_0}{\frac{1}{R}-\frac{1}{R+h+d}}\right)^2\cdot\left(\frac{r^2}{(r^2+(R+h)^2)^3}\right.$$
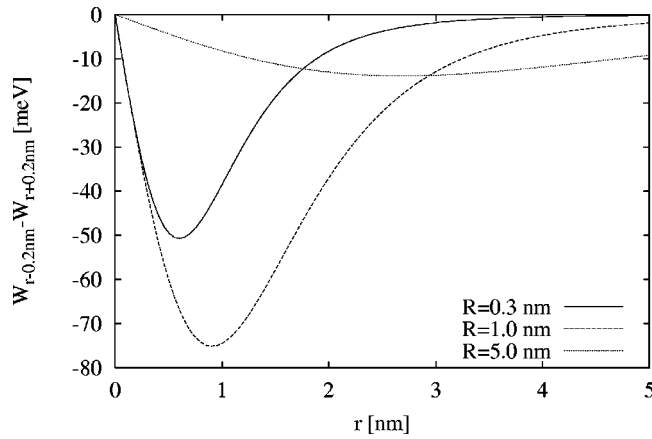
$$\left.+\frac{(R+h-z)^2}{(r^2+(R+h-z)^2)^3}\right).$$

FIG. 8. Change in energy for a 0.4 nm in-plane displacement of an induced dipole (Sb$_2$ dimer). The solid curve represents a tip radius of curvature of $R = 0.3$ nm, the dashed curve $R = 1$ nm, and the dotted curve $R = 5$ nm (tip–sample distance of $h = 1$ nm (polarizability 8.8×10^{-38} C m^2/V, $V_{bias} = 3$ V, $d_{depletion} = 10$ nm). The model results in an attractive force with a maximum at a distance approximately half of the radius of R.

FIG. 9. Change in energy for a 0.4 nm displacement normal to the surface of an induced dipole (Sb$_2$ dimer). Parameters are identical to the curves in Fig. 8. The model results in an attractive force with a maximum directly below the tip. The 0.4 nm normal to the surface was chosen for comparison to the displacement of one dimer row in the plane.

Here h is the tip surface separation, d is the width of the depletion layer, and R is the radius of curvature of the tip. The energy term W is cylindrically symmetric so only the radial distance of the adsorbate to the tip and the motion of the tip are important for the manipulation.

A rough estimate for the polarizability α is the value for a free antimony atom $\alpha = 1.1 \times 10^{-39}$ C m^2/V.[8] In general an adsorbate on the surface is expected to have a polarizability different from the free specimen (atom, dimer). Based on their diffusion studies Whitman *et al.*[6] argued that the polarizability of Cs is considerably larger on the InSb(110) surface than expected. We have done preliminary quantum chemical calculations to find α of a Sb$_2$Si$_7$H$_{10}$ cluster. The structure of this cluster is based on a single Sb$_2$ dimer on the Si(001) 2×1 reconstruction. The Sb atoms are bonded together and to two Si atoms each. Remaining Si dangling bonds are terminated by hydrogen atoms. The approximate polarizability of this cluster is 8.8×10^{-38} C m^2/V, with a permanent dipole of 2.4×10^{-30} C m orthogonal to the Sb–Sb and to the Si surface. For comparison, replacing the Sb with H leads to 6.0×10^{-38} C m^2/V and 0.4×10^{-30} C m.

The energy available to move the induced dipole in-plane is set to be the energy difference of the initial and final position $dW = W(r_{init}) - W(r_{final})$. As shown in Fig. 7 the in-plane component of the field is considerably smaller than the normal component and goes to zero below the tip. Figure 8 displays the energy gained by displacing the dipole 0.4 nm in the plane toward the tip. For comparison the energy gained by displacing an induced Sb$_2$ dipole 0.4 nm toward the tip normal to the plane is plotted in Fig. 9 as a function of in-plane distance to the tip for various tip radii.

The energy change due to the field of the STM tip has to be compared to the corrugation potential of the surface. The Sb$_2$ dimers are confined to the π chains (0.76 nm spacing) of the Si substrate by a potential barrier of 1.2 eV.[7] The displacement of the adsorbate used in the plots (0.4 nm) is motivated by a simple potential landscape: 1.2 eV confine-
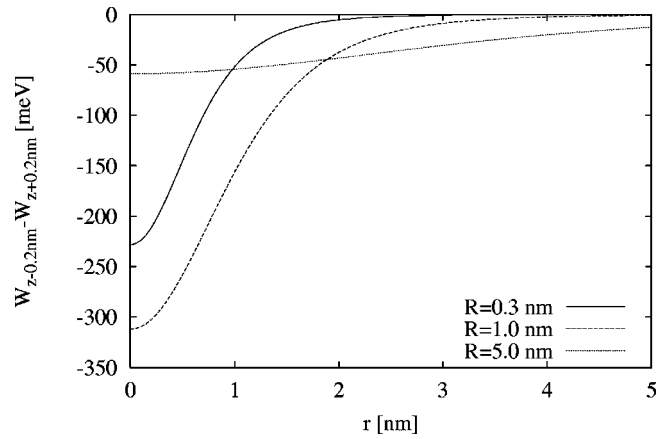
ment from the center of the π chain to the center of the π^* chain. If the potential gain due to a 0.4 nm displacement is greater than 1.2 eV the Sb$_2$ dimer would hop onto the next Si π chain ignoring the aid of thermal occupation of higher energy levels. However, assumption of an Arrhenius law for the hopping rate, $\Omega \exp(-E/kT)$, leads to the following expression for the necessary change in barrier height to double the hopping rate: $\Delta E = kT \ln 2 = 27$ meV$|_{450 \text{ K}}$.

Figure 10 shows the potential change for a permanent dipole in a field. The same displacement of 0.4 nm was chosen for comparison with Fig. 8. For the field direction used the curves reflect a repulsive force directly below the tip in contrast to the force on an induced dipole. Furthermore, in contrast to the induced dipole the force changes sign at a distance comparable to the tip radius of curvature plus the tip height over the surface, $R + h$. The energy associated with displacing a permanent dipole of the magnitude expected for
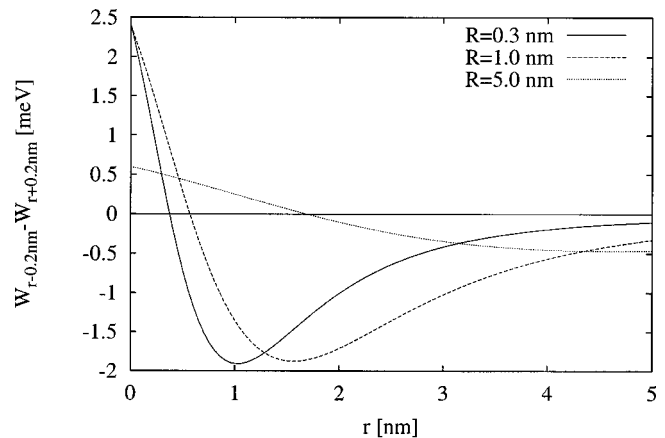

FIG. 10. Change in energy for a 0.4 nm displacement of a permanent dipole, $p = 2.4 \times 10^{-30}$ C m (other parameter identical to the other plots). Except for the region very close to the origin (set by the tip radii) the potential change is overall attractive (or repulsive for opposite field direction) with a minimum slightly further way from the origin compared to the induced dipole.

Sb_2 is at the most a few meV$\ll kT$ in contrast to the induced dipole. Hence, the contribution from a permanent dipole is small compared to the potential of the surface corrugation. In contrast to Sb, Cs is an adsorbate with a large permanent dipole compared to the induced dipole.[6]

The energy gain of a Sb_2 dimer hopping one dimer row closer to the tip in the case of an induced dipole as shown in Fig. 8 is considerably lower compared to the same displacement normal to the plane at shown in Fig. 9. Furthermore, the in-plane movement shows a maximum in force at a distance of roughly half the tip diameter in contrast to the normal component with a maximum exactly below the tip. In contrast to the permanent dipole the coupling of the normal and parallel component in the energy term of the induced dipole results in an overall attractive potential.

The depletion depth for Figs. 7–10 was chosen to be 10 nm without taking into account the effect of the dielectric or a ground plane on the field distribution at the adsorbate. The depth was only used to find the magnitude of the point charge. Placing the zero potential reference at infinity will lower the maximum energy in the dW plots by a factor of 2. Placing the zero reference at the surface will increase the energy available for a displacement of an induced dipole by a factor of 150. However, this assumption is unphysical since it implies no depletion layer and a metallic surface with a nonzero in-plane field component.

The large dielectric constant of Si, $\epsilon_{Si} = 12$, will cause a larger in-plane component of the electric field. This will affect the Sb_2 dimer on the surface since the induced field of the dielectric will partly extend into the vacuum. The field distortion due to ionized dopants should be small, since we work with fairly low doped substrates, and the amount of charge at the tip even with a depletion zone reaching to infinity is larger than ten electrons. The dominant unknowns are the polarizability of the Sb_2 dimer on the Si(001) surface and the tip radius and shape.

It is necessary to investigate the importance of vibrational heating as a source of the Sb_2 manipulation. Local heating due to the STM tip can cause adsorbate motion as discussed in Ref. 14. Heating due to inelastic tunneling was successfully applied to two experimental systems: xenon on a metal surface at low temperature and hydrogen on Si at room temperature. The tunneling current creates in both cases a substantial temperature increase of the adsorbate compared to the substrate temperature. The model discussed in Ref. 14 can also be applied to Sb_2 on Si. The atomic mass of Sb is similar to Xe and so the same vibrational frequency (2.5 meV) should be a good approximation. For this low frequency coupling to phonons should be the dominant process that limits the lifetime of the excited state. Using the speed of sound and density of Si and the atomic mass of Sb we find a vibrational damping rate for Sb on Si of 1/15 ps (slightly faster than in the case of xenon). Following the argument of Ref. 14 this results in a temperature elevation of the adsorbate of ≈ 0.15 K at 300 K for a current of 5 nA with a large inelastic tunneling fraction of 10^{-3}. The effect is much stronger for hydrogen: the low mass results in a high frequency vibration, 2084 cm^{-1},[14] with a much longer lifetime since this is above the highest phonon modes of the substrate. At room temperature vibrational heating of Sb on Si (0.012 meV) is a small effect compared to the change in energy due to the tip–dipole interaction (10 meV for a macroscopic tip).

VI. DISCUSSION

The energy available for manipulation due to an electric field-based interaction between tip and adsorbate is only on the order of the thermal energy leading to a low probability of directed hopping. If the enhanced hopping rate due to the tip is small compared to the existing diffusion the asymmetry introduced due to the tip motion will not lead to directed motion since the hopping rate is too low to follow the tip. The change in potential landscape needs to be local as indicated by the 0.4 nm shift used in the calculations above. If the potential barrier of the corrugation is lowered on both sides of the adsorbate with respect to the tip position only a larger total hopping rate is to be expected as observed in Fig. 4. As shown in Fig. 8 an ultrasharp tip of $R = 0.3$ nm can lead to a locally large enough field to cause directed manipulation but already a tip of $R = 5$ nm leads to a low gradient causing a lowering of the barriers with a small asymmetry. Thus, only an ultrasharp tip can lead to directed hopping.

A cylindrically symmetric potential/force due the tip, Fig. 8, can lead to an anisotropy in the manipulation due to the motion of the tip. If the dimer has hopped along the direction of tip motion an additional hopping event is more probable than in the case where the dimer has hopped in another direction. This asymmetry will appear if the attraction of the tip is strong enough to drag the adsorbate along. An enhanced isotropic hopping rate (ignoring preferred directions due to the substrate) is the result of a weak interaction since the adsorbates cannot follow the tip. This symmetry can be broken to an extent by a low loop-gain scan, enhancing the field on one side of the dimer as discussed above. The force on an induced dipole is attractive as shown in Fig. 8, resulting in a hop toward the tip which is consistent with the negative average of the relative hopping rate Δ in Fig. 5. The high loop-gain experiments have a positive average indicating a small tendency to hop with the tip as argued in the beginning of the paragraph. We still need to explain the origin of the large scatter in Fig. 5.

There is another way to create an asymmetry in the direction of adsorbate hopping. If the termination of the tip is not symmetric, the gradient on the "front side" of the tip can be considerably different from the "backside" of the tip. This situation would either favor an invasive front- or backside of the tip breaking the symmetry of adsorbate movement. The adsorbate can in principle either hop toward the tip before the tip passes over it or afterwards, resulting in a motion with or against the tip direction. If the tip is symmetric and the probability for a second hop low this will lead to zero net movement. However, if the tip is not symmetric, the force of the front side of the tip can be different from the backside.

This will favor motion along with, or against, the direction of motion of the tip.

The magnitude of the gradient seen by the Sb_2 dimer will be dominated by the last few atoms on the effective apex of the tip, the microtip. A microtip, which extends only few atoms, dominates the field gradient on the few nm length scale. The local field is not screened on the length scale of the microtip deviation from the macroscopic tip, as has been shown by calculations[15] of the field profile of a ''blunt'' tip with an extension of atomic dimensions. At the current time microtips cannot be fabricated, they are created by microscopic changes of the tip during scanning like a rearrangement of the tip apex or adsorption of particles from the surface onto the tip. It may also already be altered after establishing the initial tunneling current due to the close proximity to the surface (large current, feedback overshoot). This explains that the gradient of the tip field, which is determined by the termination of the tip, cannot be reproduced in a controlled way. Changes in the microscopic tip termination can be observed by field ion microscopy.[16] We did not have this technique at our disposal but such a study could further confirm this model. A microtip with a certain symmetry will dominate a series of scans resulting in net movement or just enhanced hopping, as shown in Fig. 5. This lack of control over the symmetry of the microtip can thus explain the large scatter observed in the net hopping direction.

On substrates with a smaller corrugation potential a field-based manipulation technique also does not lead to atomic scale manipulation. In this case the confining potential of the adsorbate on the surface is smaller. Nevertheless, an atomically sharp tip termination is necessary to create an attractive potential that is localized to a few nanometers. The experiments by Whitman *et al.*[6] showed that field induced Cs movement on 3:5 semiconductors is possible but not on the sub 10 nm length scale. Single atom manipulation to create an artificial structure is not possible in this system. Short range interactions utilized in Refs. 1–3 are well suited for work on the atomic length scale.

VII. CONCLUSION

In summary, we have achieved local directed manipulation which is based on the electric field of the STM tip. Under good conditions the manipulation leads to directed hopping with an asymmetry ratio of up to two. Models for the manipulation based on an induced and permanent dipole were considered and specifically evaluated for the Sb_2:Si(001) system. We found that the energy that can be gained by an in-plane movement in the tip field is only on the order of the thermal energy if one assumes tip shapes that are externally controllable, i.e., no microtips. An asymmetric microtip is necessary to achieve a field distribution resulting in net movement of the adsorbates. We conclude that a field-based technique is only suited for manipulation with nm precision when a controllable microtip is available, which is not yet the case.

[1]S. J. Cheny, L. Huang, and J. Weaver, Appl. Phys. Lett. **72**, 2698 (1998).
[2]A. Dunn, P. Beton, and P. Moriarty, J. Vac. Sci. Technol. B **14**, 1596 (1996).
[3]D. Eigler and E. Schweizer, Nature (London) **344**, 524 (1990).
[4]I.-W. Lyo and P. Avouris, Science **253**, 173 (1991).
[5]T. Hashizume, S. Heike, M. Lutwyche, S. Watanabe, K. Nakajima, T. Nishi, and Y. Wada, Jpn. J. Appl. Phys., Part 2 **35**, L1085 (1996).
[6]L. Whitman, J. Stroscio, R. Dragoset, and R. Celotta, Science **251**, 1206 (1991).
[7]Y. Mo, Phys. Rev. Lett. **71**, 2923 (1993).
[8]R. Weast, *Handbook of Chemistry and Physics* (Chemical Rubber, Boca Raton, FL, 1982).
[9]L. Bartels, G. Meyer, and K. Rieder, Phys. Rev. Lett. **79**, 697 (1997).
[10]M. Richter *et al.*, Phys. Rev. Lett. **65**, 3417 (1990).
[11]O. Albrektsen, H. Salemink, K. Morch, and A. Tholen, J. Vac. Sci. Technol. B **12**, 3187 (1994).
[12]Y. Mo, Phys. Rev. Lett. **69**, 3643 (1992).
[13]Y. Mo, Science **261**, 886 (1993b).
[14]R. Walkup, D. Newns, and P. Avouris, in *Atomic and Nanometer-Scale Modifications of Materials: Fundamentals and Applications*, edited by P. Avouris (Kluwer Academic, The Netherlands, 1993), pp. 97–109.
[15]N. Lang, A. Yacoby, and Y. Imry, Phys. Rev. Lett. **63**, 1499 (1989).
[16]K. Sugihara, A. Sakai, Y. Akama, N. Shoda, Y. Kato, H. Tokumoto, and H. Murakami, Rev. Sci. Instrum. **61**, 81 (1990).