

## Nanomanipulation Using Only Mechanical Energy

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We present the first computational study targeting the nanomanipulation capability of dynamic surface force microscopy. Using a very simple but challenging model, an antisite defect on a III-V(110) surface, we show how the defect can be manipulated in both the attractive and the repulsive modes and identify the role of the tip-sample interaction: either lowering the barriers or pushing the system over a high stress state using exclusively the mechanical energy stored in the oscillating cantilever. Our study also sheds light on other key issues, such as chemical resolution, explaining why vacancies are the only defects imaged in topography, and dissipation contrast formation, identifying a physical mechanism to explain the intriguing small shift between topographical and damping images.

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Over the last decade dynamic surface force microscopy (DSFM) has developed to a key experimental technique for application in nanotechnology [1]. Its atomic resolution capability is routinely used for obtaining atomic-scale images in UHV of insulating, semiconductor, and metallic surfaces alike [1]. The atomic-scale image formation mechanisms, especially in the simplest frequency modulation mode, have been relatively well understood [2–5], while the origin of the dissipation contrast mechanism [1] and chemical resolution [6] still remain a challenge. Concerning atomic-scale manipulation, although the scanning tunneling microscopy (STM) has been the method of choice for vertical and lateral manipulation of individual atoms [7], molecules [8], and bonds [9], DSFM can overcome its fundamental limitation to conducting samples and pave the way to atomic or molecular nanomanipulation for the widest range of materials.

Unfortunately, very little experimental and no theoretical work was done in the area of nanomanipulation with DSFM. Only very recently was, for the first time, DSFM used for vertical [10] and also lateral [11,12] manipulation of single atoms on semiconductor surfaces. These remarkable experiments go beyond the lateral displacement of physisorbed or weakly adsorbed atoms on top of a surface and show that manipulation of atoms that are strongly chemisorbed or even part of the surface, including removal and deposition of single atoms without further surface damage, can reproducibly be performed using only mechanical energy stored in the oscillating cantilever in DSFM. Thus, we are facing a strong short-range tip-sample interaction regime that has not been properly explored before, either experimentally or theoretically. Previous theoretical studies have focused on either the voltage induced vertical transfer [13] or the lateral manipulation of single adatoms with the tip of an STM or static atomic

force microscope [14]. These studies do not provide significant clues about the basic questions behind the vertical manipulations discussed above. For instance, can they be performed in both the attractive and the repulsive interaction regimes? Or, in other terms, is the basic atomistic mechanism related to a lowering of the barriers by the presence of the tip (the bonding between the manipulated atom and the tip is lowering the energy of the transition state), or is it a purely mechanical effect where the atom is pushed over the barrier by the tip following a high stress state, or is it a result of a local heating associated with the energy dissipated in the periodic approach and retraction of the tip during the cantilever oscillation?

This Letter aims to fill the gap and, using computational tools to simulate the tip-surface approach curves [1], to shed light on the atomistic mechanisms behind the nanomanipulation using only the mechanical energy of the oscillating cantilever. The computed total energy curves can easily be converted to measurable site-specific frequency shifts or dissipation [1,2]. In particular, we want to address basic questions that can guide the experimentalists in the design of manipulation protocols, such as the feasibility of manipulation in both the attractive and the repulsive short-range interaction regimes, the role of tip reactivity, the relevant distance ranges for imaging and manipulation, and the possible relation between manipulation and dissipation atomistic processes that are both nonconservative.

To this end, we use a very simple but challenging model system, an anionic antisite defect on a III-V-(110) surface. This system sets a very stringent test on single-atom manipulation without further surface damage, given the short interatomic distances. On the other hand, it provides a strong versatility making manipulation processes other than the usual atom/vacancy removal possible. We dem-

onstrate that the defect, with two stable configurations that differ by  $\sim 1$  Å in the normal direction, can be manipulated with the DSFM tip to switch its position from one minimum to the other. In particular, the role of tip reactivity and the attractive or repulsive character of the interaction on the feasibility of this process can easily be extrapolated to other systems. Furthermore, comparing the interaction for the anion in these different bonding environments, the perfect surface and the two defect configurations, we address the chemical identification capabilities. Finally, we show that the defect can be used as an initiation point to form larger-scale defects, such as removed nanowires.

Our model is based on the division [3,15] of the tip into a macroscopic part that contributes mainly the long-range background interaction and a nanotip which is responsible for short-range forces. The background long-range interactions can be separated experimentally [16]. Moreover, these interactions are too long ranged to account for motion of individual atoms. For that reason we focus only on the short-range interaction of the model nanotip with the sample. Si tips are customarily used in the experiments [10]. We describe the nanotermination of the tip by a well tested 10-atom Si nanoasperity saturated at the base by H atoms [3]. The apex and the three nearest-neighbor Si atoms of the tip are allowed to relax. The main characteristics of this highly reactive Si nanotip is the presence of one singly occupied dangling bond sticking out of the tip apex. We have also explored the influence of an oxide layer and the possibility of surface contamination considering other tip terminations. We consider explicitly the InP(110)- $1 \times 1$  surface, which we model in slab geometry by  $4 \times 3$  primitive unit cells and slabs five layers thick with three free and two fixed bulk-terminated layers (the bottom layer H-saturated). The image interaction in the  $z$  direction is minimized by a vacuum layer at least 6 Å thick. The energies and forces were calculated within the density functional theory (DFT) in its plane-wave pseudopotential formulation [17] using the CPMD suite of codes [18]. All atoms were described by pseudopotentials [19]. We use the gradient corrected Perdew-Burke-Ernzerhof functional for the exchange-correlation energy [20]. The wave functions were expanded at the  $\Gamma$  point of the Brillouin zone with a plane-wave cutoff of 10 Ry (25 Ry when first-row elements, such as oxygen, are used; see below).

The model system is built by substituting one of the surface In atoms by P to form an anionic antisite defect. This defect is commonly present on the III-Vs [21]. We found two stable geometries for the defect. One, previously described in the literature [22] with the defect positioned roughly in the plane of the other phosphorus atoms (ground-state geometry), and the other where the defect atom is positioned well below (local-minimum geometry; Fig. 1). We label these geometries  $g$  and  $l$ , respectively. Constrained total energy calculation along a path where the defect atom is moved from the  $g$  to the  $l$  position with all

the other free atoms allowed to relax reveals that the defect atom moves vertically in a double-well potential with  $\Delta U \sim 0.5$  eV and  $\Delta U_b \sim 0.08$  eV (Fig. 1). Hence, the defect could be stabilized in the local minimum. Moreover, as shown in Fig. 1, the existence of the local minimum is an exclusive property of the defect site absent from a perfect phosphorus site ( $p$  site).

We now show how the defect can be manipulated from one minimum to the other and determine the influence of the character of the interaction (attractive or repulsive) and the tip reactivity in the process. In order to flip the defect from the local into the global minimum ( $l \rightarrow g$  process), we first consider our standard model Si nanotip (see Fig. 2). Within our limited search we have observed the desired nanomanipulation only with the model tip positioned over the trench between the In-P chains close to the defect. The potential energy surface (PES) for that process is shown in Fig. 2. Flipping the defect into the ground-state geometry may occur in both the attractive and the repulsive modes, as shown by the two approach-retraction cycles displayed in the upper panel of Fig. 2.

In the attractive mode, a small reduction of the tip-surface distance ( $\sim 0.5$  Å) from the stable imaging range leads to the manipulation. The  $l$  site is bonded to the apex atom only by a single bond. The tip acts as a catalyst that (1) lowers or eliminates the energy barrier  $\Delta U_b$ , and (2) by forming a loose bond with the defect atom increases the barrier  $\Delta U$ . Elimination of the local minimum in the PES on tip approach (Fig. 2) leads to lifting the defect into the  $g$  site and nanomanipulation. In the repulsive case the defect atom is bonded into the nanotip structure by a double bond (Fig. 2), and the PES is extremely complicated, combining different elastic and plastic deformation stages. Each dis-

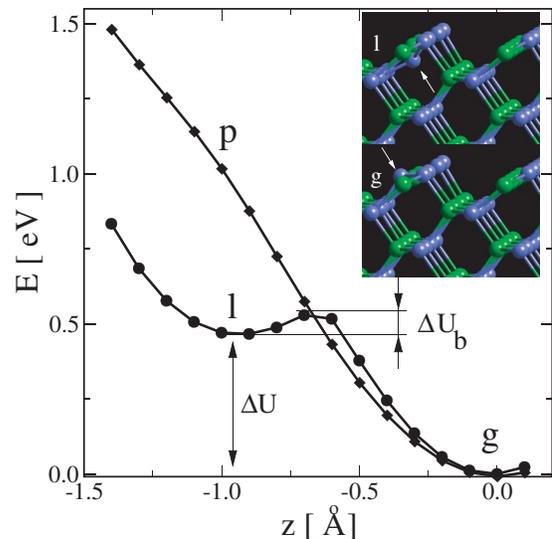


FIG. 1 (color). Potential energy surface for the P antisite defect (dots) and P atom in a perfect In-P chain (diamonds) as the atom moves along surface normal. The insets show ball-and-stick models of the  $g$  and  $l$  structures.

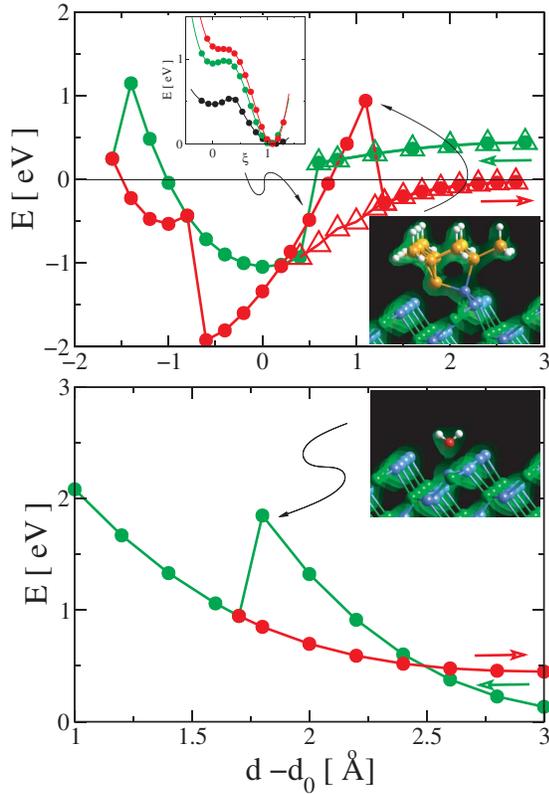


FIG. 2 (color). PES for nanomanipulation. Upper panel:  $l \rightarrow g$  process using model Si tip. Lower panel: reverse manipulation using model  $\text{H}_2\text{O}$  tip. Green: tip approach; red: tip retraction. Two tip approach-retraction cycles are shown in the upper panel. Flipping in attractive (repulsive) regime: open triangles (solid dots).  $d - d_0$  is the tip-surface distance [3]. The insets show ball-and-stick models with superimposed isosurfaces of constant valence electronic charge density at the point of PES indicated by black arrows. PESs for flipping the defect with the tip positioned before (green), after (red) the discontinuity and in infinity (black) are shown in the inset of the upper panel. The reaction coordinate  $\xi$  was determined by linear interpolation between structures before and after the discontinuity.

continuity observed on the total energy curves corresponds to the plastic transition to a new stable configuration with the formation or breaking of a tip-sample bond, a bond in the nanotip, or a bond in the surface [23].

We were unable to perform a reverse manipulation ( $g \rightarrow l$ ) with the same model tip. This is most likely because the reactive Si nanotip always binds to the defect atom, which then follows the tip retraction leaving the defect in the  $g$  structure. Other tip configurations devised to simulate tip contamination, where the Si apex atom was replaced by either In or P, although less reactive, provide the same results. For that reason we have decided to use a purely repulsive tip. One very simple-minded tip functionalization is to consider an oxidized Si tip. Unfortunately, to model the oxide layer on a Si substrate is a problem in its own right. Therefore we have considered the simplest model, namely, a  $\text{H}_2\text{O}$  molecule that has been shown to

represent a relatively close mimic of an apex formed by an oxide layer [5]. The result is shown in Fig. 2. This tip, indeed, represents a pure repulsive tip-sample interaction and a gentle nanoindentation of the surface leads to flipping the defect atom into the local-minimum geometry ( $g \rightarrow l$  process).

The three different ways the P atom is bonded on the surface also provide a critical test on a key issue in DSFM: the capability to achieve chemical resolution. The computed approach scans over the three different P sites [23] (not shown) indicate that, at larger tip-sample distances, the bonding strength decreases roughly with the height of the P atom ( $p$ ,  $g$ , and  $l$ ). The comparison with the approach curve on the In atom shows that the antisite in its stable configuration cannot be distinguished from the nearby In atoms unless we come really close to the surface and enter the short-range repulsion regime. This theoretical result can explain why vacancies are the only point defects observed in the DSFM images of III-V(110) surfaces [24] in the topographic mode.

The complicated total energy landscapes and their strong dependence with tip position revealed by our calculations have important implications for nonconservative processes such as manipulation and energy dissipation. As discussed above, a scan on top of a  $g$  site leads to a curve indistinguishable from that on top of an In site. However, moving the tip  $0.2 \text{ \AA}$  from the on-top position toward the In-P chain and allowing the tip into repulsion leads to a completely different result shown in Fig. 3. As can be seen, the number of discontinuities lead to a complicated hysteresis loop in the approach-retraction cycle that results in a strong dissipation. Each of the discontinuities corresponds to a motion in a double-well potential where one minimum disappears as the tip approaches the surface. This is at the heart of the theory of dissipation images caused by nonconservative effects similar to those leading to nanomanipulation. Tip-induced instabilities,

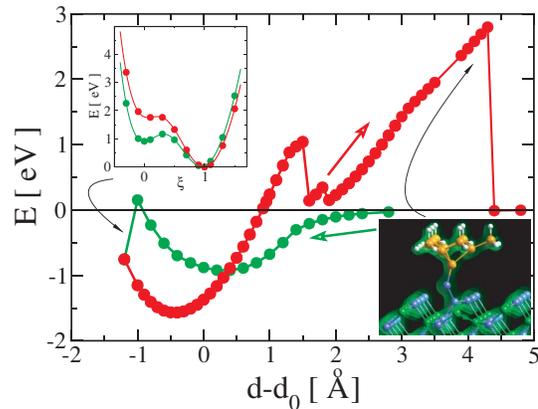


FIG. 3 (color). PES for a P atom in the  $g$  geometry. Note the discontinuities caused by soft modes. Left inset: PES for tip position before (green) and after the discontinuity (red). Right inset: pulling a nanowire. Color convention as in Fig. 2.

such as “soft” vibrational modes [1,25], are typically associated with an instability of a surface atom perpendicular to the surface. The soft mode we discuss here (Fig. 3) is instead caused by a lateral tip apex instability. An even more complicated scenario occurs at the end of the cycle, where the enormous  $\sim 3$  eV discontinuity is caused by formation of a P-P-P nanowire that ultimately bounces back onto the surface and rebuilds the chain structure. This would lead to a very strong dissipation signal from the  $g$  site if the tip is allowed into repulsion.

We note that all processes we observe here are “exothermic” with the energy dissipated presumably primarily into phonons. The interplay between the possible local overheating caused by this energy dissipation and the dynamic nature associated with the oscillating cantilever may seem to call into question our static,  $T = 0$  approach for the analysis of manipulation in DSFM. However, typical oscillation frequencies ( $\approx 100$  kHz) are low enough to allow for a complete thermalization of the system well before the following tip approach. On the other hand, the very localized character of surface modification shown by the manipulation experiments (no further significant damage is visible after removal of an atom or vacancy) rules out a very strong overheating. Under these conditions, although a temperature-assisted enhancement of barrier crossing between different bonding configurations cannot be completely discarded, our results do show that the tip-sample interaction can have a more important role, either lowering significantly the barriers or pushing the sample atoms over a high stress state using the stored mechanical energy.

In summary, we have performed the first DFT simulation study of the DSFM nanomanipulation, including processes other than the usual atom or vacancy removal, on a challenging model system, an anionic antisite defect on a III-V(110) surface. We have shown that some single-atom manipulation processes can occur in both attractive and repulsive modes, with the tip-sample interaction playing different roles: either lowering the barriers or pushing the system over a high stress state using the mechanical energy stored in the oscillating cantilever. In addition, we have addressed other key issues in DSFM, such as chemical resolution [6] and dissipation image formation [1]. Our results show that although antisite defects cannot be easily distinguished from the nearby cation atoms in the frequency shift images, explaining why only vacancies are observed experimentally, they should provide a distinctive dissipation signal. Moreover, the lateral tip apex instability we have identified provides a physical dissipation mechanism to explain the intriguing small shift between topographical and damping images observed [1,2].

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