

## Cyclic Single Atom Vertical Manipulation on a Nonmetallic Surface

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Cite This: *J. Phys. Chem. Lett.* 2021, 12, 11383–11390

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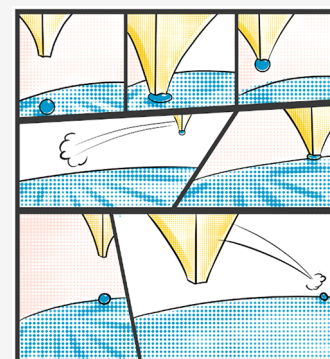


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Supporting Information

**ABSTRACT:** Motivated by the quest for experimental procedures capable of controlled manipulation of single atoms on surfaces, we set up a computational strategy that explores the cyclical vertical manipulation of a broad set of single atoms on the GaAs(110) surface. First-principles simulations of atomic force microscope tip–sample interactions were performed considering families of GaAs and Au-terminated tip apices with varying crystalline termination. We identified a subset of tips capable of both picking up and depositing an adatom (Ga, As, Al, and Au) any number of times via a modify–restore cycle that “resets” the apex of the scanning probe to its original structure at the end of each cycle. Manipulation becomes successful within a certain window of lateral and vertical tip distances that are observed to be different for extracting and depositing each atom. A practical experimental protocol of special utility for potential cyclical manipulation of single atoms on a nonmetallic surface is proposed.



Since the invention of scanning probe microscopes in the 1980s,<sup>1–3</sup> there has been a series of astounding advances made in our ability to image, probe, and manipulate matter at the single atom—and, more recently, single chemical bond—limit. Individual atoms and molecules have been pushed, pulled, poked, prodded, or otherwise picked-and-placed by using a variety of manipulation schemes underpinned by a range of physicochemical interactions.<sup>4</sup> Building on the substantial achievements of scanning tunneling microscopy (STM) in atomic and molecular manipulation,<sup>5–12</sup> dynamic force microscopy, with both conventional silicon cantilevers<sup>13–15</sup> and the qPlus sensor design introduced by Giessibl,<sup>16–19</sup> has led to a step change in precision and, equally importantly, substantially extended the palette of manipulation mechanisms available to probe for microscopists. These now include, in particular, the controlled application of mechanochemical force.<sup>11,12,20</sup> This type of mechanochemistry strategy reaches its apogee in the direct, bond-by-bond, and chemical synthesis of single molecules, as described in, for example, the pioneering papers of Pavilcek et al.<sup>21,22</sup>

The effective rate-limiting component in any probe microscopy technique, however, is of course the probe itself; coercing the apex of the tip into the precise atomic or molecular structure required to image or modify matter at the atomic level is a major bottleneck when it comes to increasing the efficiency of the technique. Gross et al.’s<sup>23</sup> demonstration that tip functionalization via the attachment of a CO molecule could dramatically improve image resolution for force microscopy has led to the widespread adoption of that protocol, particularly in the qPlus variant.<sup>19</sup> Strategies for tip functionalization other than CO attachment have also been used very successfully.<sup>24–26</sup> It is safe to say, however, that

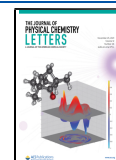
control of the tip apex remains an especially challenging aspect of scanning probe microscopy. Machine-learning approaches have exciting potential when it comes to automating tip control,<sup>27–29</sup> but the development of strategies to optimize the probe apex requires a more considered combination of experimental and theoretical input. In particular, the atomic, chemical, and electronic structure of the tip apex not only establish image quality but also fundamentally underpin our ability to manipulate atoms and molecules. For example, relatively small changes in the orientation of a tip-terminating atomic orbital can have significant ramifications on single atom manipulation.<sup>30</sup>

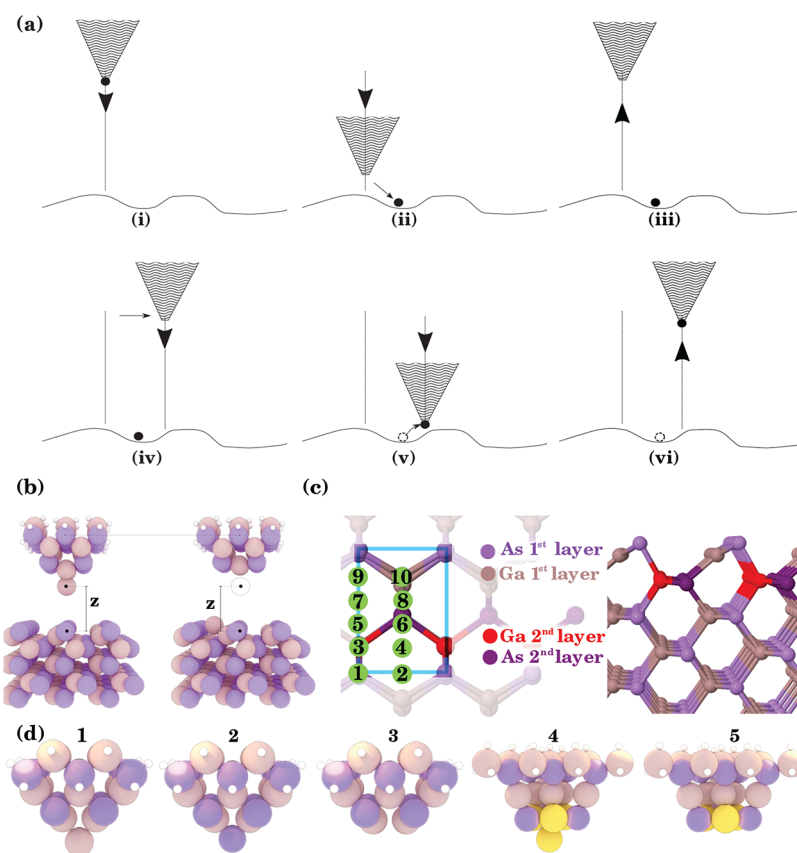
Pushing the limits of single atom control beyond the creation of 2D structures and toward the fabrication of more complex nanostructures necessitates a careful consideration, and systematic sifting, of the very wide structural space associated with the large family of potential tip states. At a minimum, it requires that the tip be able to pick up an atom at one position on the surface and subsequently deposit it elsewhere, that is, to carry out so-called “vertical” manipulation of atoms in a routine and reliable manner, with atomic resolution retained throughout the entire process. Sugimoto and co-workers<sup>31</sup> introduced a key mechanism for manipulation of this type: the “vertical interchange” protocol.

Received: July 14, 2021

Accepted: August 3, 2021

Published: November 16, 2021





**Figure 1.** (a) Schematics of the full single atom deposition–picking cycle. The original atomically sharp tip in (i) is recovered in (vi). (b) Definition of the tip–surface distance  $z$  used in our simulations. (c) Optimized GaAs(110) surface: top view (left) with the lateral grid points indicated in green and side view (right). (d) GaAs tips based on the GaAs(001) surface with Ga (tip 1) and As (tip 2) atoms at their apexes and the common blunt tip 3 without those apex atoms. Doped GaAsAu tips based on the GaAs(111) surface, with (tip 4) and without (tip 5) the Au apex atom. Pale pink, purple, yellow, and white atoms are gallium, arsenic, gold, and hydrogen, respectively.

Subsequently, a number of other vertical manipulation strategies have been reported.<sup>12,26,32,33</sup> However, using the *same tip* to manipulate different types of atoms on a semiconducting surface *repeatedly* during the same experimental run (and hence with the same tip) still remains elusive. The atomic manipulation process described below represents a new and important addition to the class of vertical manipulation methods, with an ability to manipulate a wide class of different atoms individually with the same tip within the same experimental run.

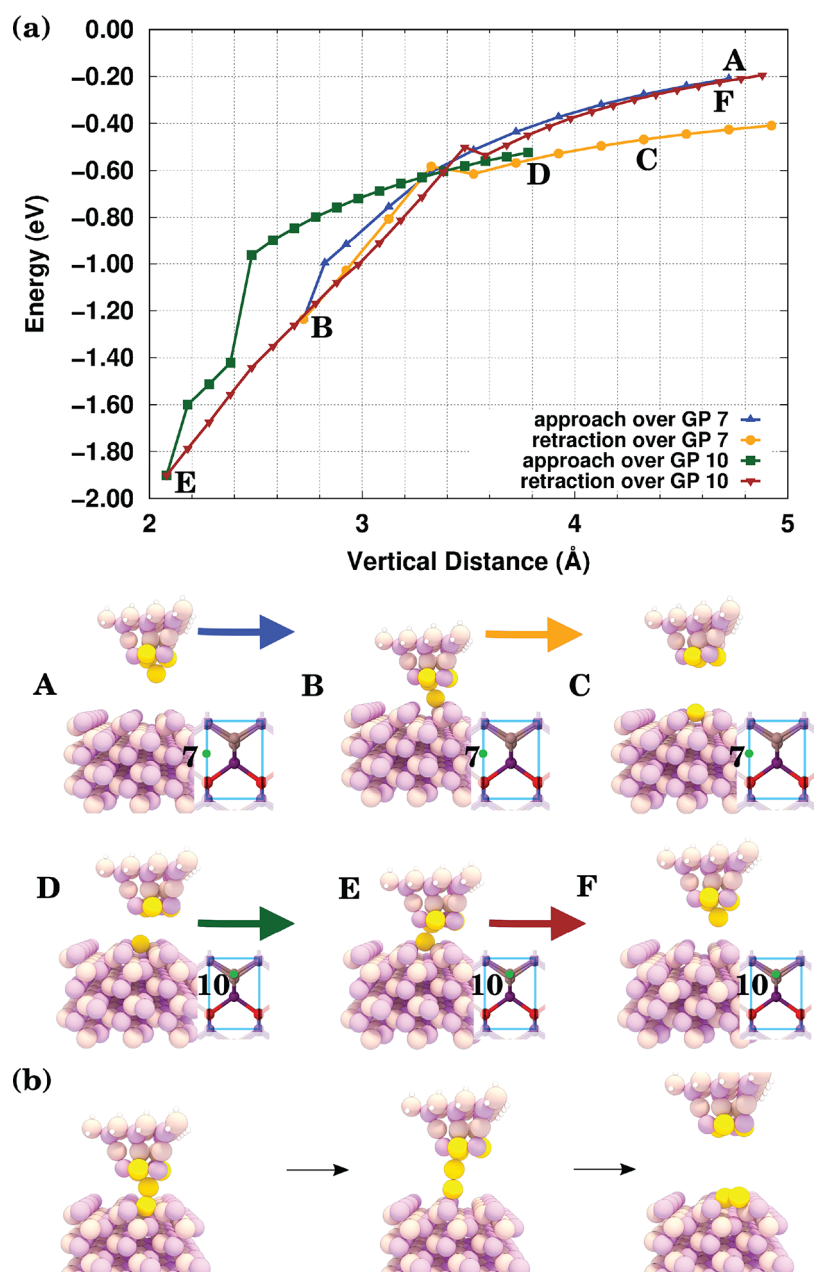
An obvious advantage of the vertical manipulation protocol is that it does not require any tunnel current or application of a voltage pulse (and therefore works on insulating surfaces) and that because it is a vertical exchange mechanism the material can be moved from anywhere on the surface unlike in lateral manipulation modes.

In searching for tip types that are capable of cyclical (i.e., structurally reversible) manipulation, we focused here, using exclusively a theoretical approach based on *ab initio* density functional theory (DFT) calculations, on broad structural features, dynamics, and properties rather than on specific atomistic detail as the latter is difficult, if not impossible, to replicate in experiment. Remarkably, our DFT calculations have identified a class of tips that not only enable cyclical manipulation but also are chemically nonspecific: with these tips a variety of atoms, including Au, Ga, As, and Al, can be picked up and dropped, with atomic precision, returning the tip apex to its original structure in each case. We predict an

energy–distance variation for this tip type that can be used in experiments as a characteristic signature of its presence. And, most importantly, on the basis of our theoretical predictions, we discuss possible ways in an experiment of fabricating such types of “self-restoring” tips and performing the manipulation experiments with them.

The entire remove–deposit cycle can be divided into a number of elementary movements of the tip, as summarized in Figure 1a: (i) An atomically sharp tip is located above a specific lateral position on the surface. (ii) The tip is driven into the surface within a specific window  $\Delta z$  of tip heights, and the apex atom jumps from the tip to the surface, becoming a surface adatom while the tip becomes blunt. (iii) Then the tip is retracted keeping the same lateral position; we have obtained a reactive blunt tip that can perform manipulation events from now on. (iv) The blunt tip is moved to a different lateral position on the surface next to a surface adatom we intend to pick up. (v) Another approach is performed at a certain lateral position, and at a very close tip–surface distance the atom jumps from the surface to the tip. (vi) The tip is retracted again, recovering the original structure. The picked atom can now be deposited somewhere else on the surface (steps i–iii). This way the full vertical manipulation cycle is performed.

In practice, in each approach–retraction process the tip is positioned in a certain way with respect to either the atom to be picked up or the lattice site where the apex atom is to be dropped. Approach–retraction simulations were performed for many lateral tip positions and for a range of approaching



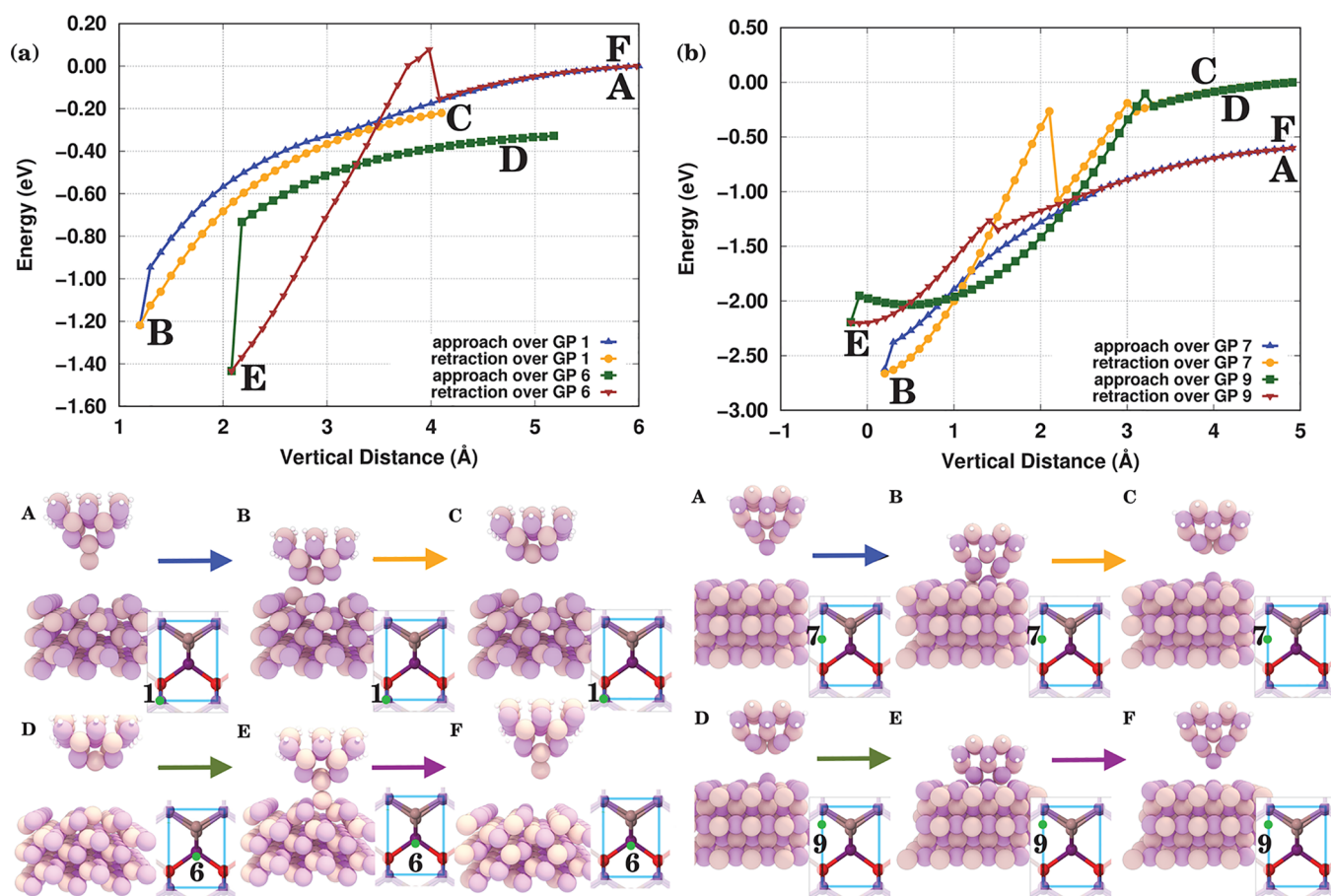
**Figure 2.** (a) Energy curves (top panel) and the corresponding geometries (bottom panels) at the characteristic points of the full picking–deposition cycle of the gold atom performed with the GaAsAu tip. (b) Deposition of a second Au adatom, next to an existing one, forming a dimer, with the hybrid GaAsAu tip. The grid point (see Figure 1c) over which the tip approaches the surface is indicated in each case by the green dot inside the unit cell (blue square) drawn next to the respective geometries.

distances (see the Supporting Information). The simulations enabled us to predict specific changes to the surface and the tip during its oscillations for a range of approach heights, including a very close approach when the body of the tip literally penetrates into the surface. In particular, we can predict if an atom from the apex of a tip is deposited on (or picked up from) the surface or not, and at which lateral position, and within which height window this will happen.

In all simulations the tip–surface distance  $z$  was defined as the distance between noninteracting tip apex and surface. Ten equally spaced lateral positions above the GaAs(110) surface were chosen as shown in Figure 1c to cover the area of the primitive surface unit cell. These positions are numbered in Figure 1c and will be referred to in the text correspondingly.

We have considered a set of different tips composed of Ga, As, and Au atoms, some of which were found to be able to pick up an atom into their apex position and deposit it back onto the surface. The first set of tips consists of Ga and As atoms only (see Figure 1d, tips 1–3). Tip 3 is a common base for tips 1 and 2 and can manipulate more than one species. The base of tip 5 shown in Figure 1d is obtained from the hybrid GaAsAu tip 4 by removing the apex Au atom; its upper GaAs base is formed from the GaAs(111) surface.

We shall only consider manipulating *adatoms* on the surface as extracting atoms from the pristine surface with any of the tips appears to be impossible (see the Supporting Information for details, including the case where swapping between the tip apex atom and the topmost As surface atom is demonstrated).



**Figure 3.** Energy curves (top panels) and the corresponding geometries (bottom panels) at the characteristic points of the full picking–deposition cycle for (a) gallium and (b) arsenic atoms. In both cases the same blunt tip was used; that is, the tips in (a, b) only differ by their apex atom.

We shall first focus on the four-gold-atom-doped GaAs tip 4 of Figure 1d. At the tip apex we have an Au atom. Our calculations show that this atom can be deposited on the surface within a window of heights of  $\Delta z = 2\text{--}3\text{ \AA}$  above grid points (GPs) 4, 5, and 7. Once the tip has deposited its apex atom, it becomes blunt with only three gold atoms left that are exposed to the surface (Figure 1d, tip 5). As explained below, we find that this blunt tip is capable of collecting another gold adatom from the GaAs surface, and in doing so it recovers its original structure, ready to deposit again the acquired gold atom, thereby performing a complete pick–deposit cycle. We demonstrate this by placing a gold adatom on the surface and then performing with the blunt tip approach–retraction cycles over each of the ten grid points (GPs). After performing retraction from different heights  $z$ , we find that for some of them (specific window of turning points heights  $z$ ) the gold adatom can be collected by the blunt tip when placed above GPs 9 and 10. In doing so the original tip structure of Figure 1d,4 is fully restored.

The energy curves for all of these processes, together with characteristic geometries, are shown in Figure 2a. The hybrid tip is approached over GP 7 (the blue curve), and a sudden change in the energy curve appears at around  $z \approx 2.7\text{ \AA}$  due to a strong interaction between the gold apex atom and the surface, as shown in geometry B in Figure 2a. After retraction of the tip (the yellow curve), the gold atom remains on the surface (C in Figure 2a) and the tip becomes blunt. Next, we move the blunt tip from GP 7 to GP 10 to perform a new

approach–retraction cycle (sequence D  $\rightarrow$  E  $\rightarrow$  F). This time, at a lower height, two sudden changes are observed, indicating that the collection mechanism is not a single-step process (the green curve). The adatom is attached to the tip at  $z \approx 2.1\text{ \AA}$  (E in Figure 2a), and after retraction (the red curve) the Au atom stays on the tip, completing the full pick–deposit cycle. As can be seen (compare geometries A and F), the tip structure has been completely restored.

The implication of this *in silico* experiment is that a class of GaAs-based tips exists, with a few Au atoms at their apices, that can be transformed into a blunt tip by depositing a protruding gold atom. This blunt tip is capable of picking up a gold atom anywhere from the surface and then depositing it back at another location, restoring the blunt tip. This procedure can be performed, at least in theory, an arbitrary number of times, providing a proof of principle for rearranging gold atoms on the GaAs surface, one by one, with a single tip. Each elementary stage of the cycle can be performed *with full control* since we know precisely where on the surface the tip should approach the deposited atom to pick it up successfully and where it should approach the surface to deposit it back.

What makes this tip even more interesting is that it can deposit a gold atom next to another one on the surface forming a surface dimer, as shown in Figure 2b. This *in silico* experiment has particular potential in guiding and informing the experimental atom-by-atom fabrication of a 2D cluster of gold atoms on the GaAs surface.

The hybrid GaAsAu tip can, however, perform a rather limited function as it is capable of completing the full picking–deposition cycle only with gold atoms. A class of other tips exists, however, that can perform the full picking–deposition cycle with *more than one* species. This is essential if we want to eventually build nanostructures made of various species, as in this case we would need to be able to manipulate different individual atoms in a repetitive manner and with *the same* tip. We find that at least one blunt GaAs tip exists (tip 3 in Figure 1d) that is capable of reversibly picking up an atom from the surface into its apex position and then placing it back somewhere on the surface, *regardless of the chemical nature of the atom*.

The important details associated with these manipulation processes are shown in Figure 3. In the left (right) panel, manipulation of a Ga (As) atom is shown. Each state of the system during the manipulation cycle, when the tip is at either the farthest or the closest point to the surface, is designated by letters from A to F. In the top panels the energy–distance curves are given, while below these we show the geometries for the states from A to F.

As before, it is convenient to start from the atomically sharp tip 1, which is composed of the blunt tip 3 (Figure 1d), with the Ga atom at its apex. Initially, this tip is positioned above GP 1 (see point A in Figure 3a). On pushing the tip into the surface (transition A→B) (the blue curve), the apex Ga atom jumps from the tip to the surface (state B). After retraction of the tip (the yellow curve), the adatom remains on the surface, and the tip, now being blunt, still keeps the basic structure of Figure 1d,3 (state C). Interestingly, the Ga atom during this manipulation settles initially in a metastable position on the surface that is by 0.2 eV less stable than the global minimum structure. However, because of a very small energy barrier of 17 meV (see details in the Supporting Information), even at rather low temperatures, we should expect the adatom to jump rather quickly into the most stable position on the surface. Hence, we find that this procedure leads to Ga atom deposition at the most stable lattice site via a two-step process.

Surprisingly, upon a more careful investigation, we find that, in addition to the deposition path considered above, there is another pathway that does not lead to an atom being deposited. The former path is slightly more favorable at large heights ( $z \geq 3 \text{ \AA}$ ) at the onset of interaction with the surface, but as the tip gets closer to the surface ( $z \leq 2 \text{ \AA}$ ), the second path becomes more favorable (see the Supporting Information). The calculated energy barrier connecting the first path with the second, calculated at  $z = 2 \text{ \AA}$ , was found to be 0.1 eV, which will be significant at low temperatures. Hence, if appropriate experimental conditions are maintained (sufficiently low temperature), the tip relaxation during the approach will follow the former (metastable) path, eventually leading to Ga atom deposition.

We subsequently moved the blunt tip to a different lateral position (above GP 6 on the surface) and then approached almost 2.0 Å toward the surface (D → E, the green curve). One can see that at this close approach the Ga adatom, placed in the most stable geometry on the surface, jumps back to the tip (E). Next, the tip was retracted (red curve) and the original Ga-terminated tip structure fully recovered (state F, with the total energy practically identical with that of A). Hence, similar to the GaAsAu hybrid tip, the full vertical single atom manipulation cycle has been performed: deposition above one grid point and picking up at another. It is important that the

structures of the tip at the beginning and the end of the cycle are identical, meaning that this cycle can be performed any number of times, repetitively. Moreover, similar to the GaAsAu tip, the deposition of the Ga atom can be considered as a method of formation of a blunt reactive tip, with subsequent retraction–deposition cycles serving to pick up Ga atoms anywhere on the surface and deposit them elsewhere.

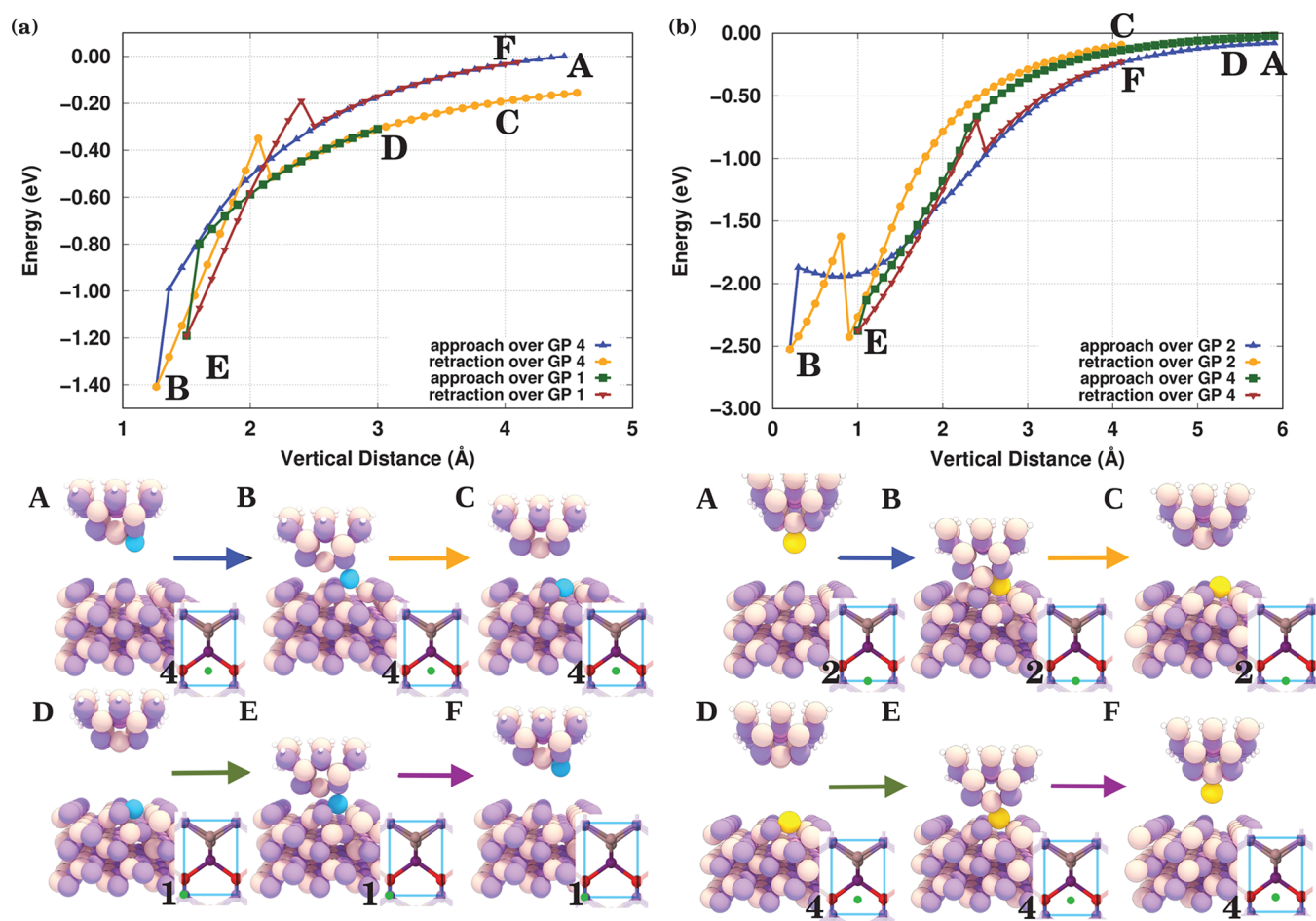
Taking now the tip of Figure 1d,2, which contains an As atom at its apex instead, a very similar-in-spirit manipulation cycle with this tip is shown in Figure 3b. Initially the tip is prepared above GP 7 and then driven into the surface (A → B), depositing its apex As atom directly in the most stable position (blue curve for approach and yellow B → C for retraction). Note that there is an abrupt change in the energy seen in the retraction curve corresponding to the atom jumping to the surface at  $z \approx 2.2 \text{ \AA}$ . Next, the tip is moved laterally above GP 9 (D), and then after the approach (D → E, the green curve) and retraction (E → F, the red curve) the cycle is repeated, during which the dropped As atom is collected back onto the tip and the latter returns to its original structure.

It is essential that in both cases of the Ga- and As-terminated tips the structure of *the blunt tip*, which serves as the common base to both tips, after the apex atom is deposited onto the surface (states C and D in both cases), is exactly the same. Hence, once the blunt tip is generated by depositing its apex atom (that is, being either Ga or As), this tip is *capable of manipulating vertically either of the two species, repeatedly and in any order*, on the GaAs(110) surface.

Although both Ga and As atoms can be manipulated by using exactly the same blunt tip, they are not manipulated in exactly the same way. A closer look at the energy curves of Figure 3 reveals some differences. First, as was stated above, Ga and As atoms have to be deposited over different grid points (1 for Ga and 7 for As). Second, for the Ga-apex tip the deposition happens around  $z = 1.2 \text{ \AA}$ , while for the As-terminated tip the jump in energy due to deposition happens at an even smaller tip–sample separation,  $z = 0.2 \text{ \AA}$ . The same situation happens for the removal process, which for Ga and As happens over grid points 6 and 9, respectively. Third, Ga deposition happens at lower  $z$  than in the removal process, while in the As case this situation is inverted. Finally, Ga is deposited into a metastable state, while the As atom bonds in the most stable state.

Intriguingly, if either of the sharp tips is brought even closer to the surface (not shown), atom deposition does not happen. For example, for As deposition over GP 7 there is a window of distances,  $\Delta z$ , where deposition occurs. If the apex is not close enough to the surface, the apex atom remains on the tip; if the tip is too close to the surface, the atom also remains on the tip upon retraction. We speculate that this is due to the repulsion between the Ga atoms at the apex of the blunt tip and those on the surface: inside that  $z$  window, the Ga atoms of the surface attract the As apex atom sufficiently strongly to retain it on the surface. If, however, the tip is moved closer toward the surface, the repulsion between the Ga atoms of the surface and of the tip dominates, and as a result, after retraction the As apex atom remains on the tip.

Furthermore, we have explored the possibility of manipulating five more species—Al, In, Sb, P, and Au—with the same blunt GaAs tip. For each of them, we have put the corresponding atom at the apex of the tip of Figure 1d,3 and repeated the same exploratory computational protocol as



**Figure 4.** Energy curves for the full picking–deposition cycle for (a) Al (blue) and (b) Au (yellow).

before. Approaching and retracting the tip from different heights at different lateral positions shows that it is also possible to deposit Al and Au. For Al (Figure 4a), we observed that the atom is adsorbed at the side of the tip. We then performed the approach–retraction protocol to find that the apex atom can also be deposited at the most stable adsorption site by approaching the tip over GP 4, and an atom can be picked up over GP 1. That means that a full manipulation cycle with the same blunt tip can also be performed for Al. We have also successfully manipulated a Au atom with the same tip, as shown in Figure 4b: the Au atom can be deposited over GP 2 (A → B → C) and collected from GP 4 (D → E → F).

The vertical manipulation of In, Sb, and P with our GaAs blunt tip has been found unsuccessful (see the Supporting Information for details).

The core result of this paper is that there is a class of AFM tips—such as the ones with a blunt stoichiometric GaAs apex—that can manipulate not only atoms of its own species but also other atoms, such as Au and Al in a repetitive manner. The implications of this are profound. It means that the same (blunt) tip can be used for picking up and depositing either of the four species, in any order and repeatedly, opening a way—at least in theory—for building nanostructures with these atoms on the GaAs(110) surface with atomic precision *within the same experimental run*. Similarly, a Au-doped GaAs tip was found that can deposit and pick up at least a gold atom, also repeatedly, suggesting that there exists a class of such tips capable of repeated vertical manipulation. It is essential to note

that manipulation of single atoms with the same tip relies on a very detailed balance of physical interactions that is especially sensitive to the particular lateral and vertical tip positions and tip model.

Our computational protocol, or a similar one, can be employed in future calculations of finding wider families of possible tips capable of described picking–deposition cycles. However, the important outcome of this work is that our conclusions pave the way to establish experimental guidelines for cyclical vertical single atom manipulations of different species on a nonmetallic surface. More explicitly, the following directives can be drawn from our work:

(i) A cyclic manipulation requires a blunt reactive tip. An example of such a tip is a GaAs cluster shown in Figure 1d,3. To fabricate such a tip, first an indentation of the tip into the surface is required until stable atomic resolution is achieved. Then, the required blunt tips can be prepared by removing apex atom(s), thereby turning them into blunt tips with enhanced reactivity. Similarly, the preparation of tip apexes with species different from those of the surface itself (as, for instance, gold-terminated tips of Figure 1d,4) require indenting the tip into surface clusters made of the desired species.

(ii) The tips must be reactive in a sense that the interaction of a surface adatom is stronger with the tip than with the surface at some lattice sites (so that this atom can be picked up by the tip) and weaker at the others (so it can be dropped). Theoretical simulations are necessary to guide the experimentalists in selecting the appropriate lattice positions for picking

and depositing adatoms. Examples of “successful” tips are provided by the blunt GaAs and the hybrid GaAsAu tips discussed here. A detailed analysis of breaking and formation of bonds could shed some light over the chemistry involved in the processes.

(iii) Because of the critical dependence of the atomic manipulation probability on the position of the tip within the surface unit cell, a 2D grid of frequency shift measurements is first required. Because of the precision required to locate the various grid points within the unit cell, drift compensation will almost certainly be necessary.

(iv) There is a certain window of tip heights  $\Delta z$  at which either of the manipulations happens.

(v) Finally, the stiffness of the tip should be comparable to that of the surface: a softer tip (e.g., a pure gold tip) would not be able to pick up atoms from the GaAs surface (see, however, the swapping mechanism considered in the [Supporting Information](#)), while a stiffer tip (e.g., a tungsten tip; see the [Supporting Information](#)) would disrupt the surface extensively, extracting atoms in an uncontrollable fashion with little hope of redeposition. Therefore, tips made of the same material as the surface, or similar, are advantageous.

The manipulation protocols require precise positioning of the tip with respect to the manipulated species (pick up) or the lattice site (deposition). In turn, this requires, at all stages of the manipulation process, that the surface can be imaged with high resolution. However, as the apex atom is lost, the tip becomes blunt and will lose this ability. This reduction in image resolution will follow an abrupt change in energy ([Figure 3](#)). Hence, the key signature of deposition of an apex atom and the primary “observable” for experimentalists is the abrupt change in the force–distance curve and the concomitant reduction in image resolution that will accompany this change. Because of its smaller radius of curvature, the deposited atom will act to “reverse image” the blunter tip. This will make the interpretation of the image contrast somewhat problematic, but nonetheless, a very distinct feature related to the deposited atom will be observed.

Because of the requirement of the precise positioning of the tip with respect to the surface, one has to rely on low temperatures or an atom-tracking system to avoid thermal drift and an ability to program all stages of the manipulation process after taking an image of the manipulating area with a sharp tip at the start of the manipulation sequence; 77 K is feasible, but 4K is preferable. Low temperatures may also be essential to fix the desired manipulation path (as is the case with Ga atom deposition). Also, it is known<sup>34</sup> that adsorbates are very easily translated laterally across the surface by the tip unless the temperatures are sufficiently low.

The key proof of principle of the cyclic manipulation process will be the readsorption of the deposited atom on the blunt tip. For Ga, this produces a striking discontinuity in the  $E(z)$  curve (compare curve D  $\rightarrow$  E in [Figure 3a](#)) associated with a change in energy of 0.75 eV when the atom returns to the tip. Accompanying this discontinuity will be a restoration of high-resolution imaging.

The identification of tips that are indefinitely “recyclable” is an exciting new addition to the atomic manipulation toolbox. Our simulations have predicted characteristic energy vs distance signatures for this type of tips, and we are hopeful that those predictions will inspire experimentalists to verify them in the near future.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcllett.1c02271>.

Extracting atoms from the upper GaAs(110) surface layer; adsorption energies and geometries of Ga and As adatoms on the GaAs(110) surface; selection of extra tips; alternative GaAs tip approaching path; Ga adatom diffusion energy barrier; deposition with pure gold tips: (i) swapping between Au tip and As surface atoms, (ii) gold thread formation on the GaAs surface; approaching–retraction cycle of GaAs tips with In, P, and Sb at the apex; approaching–retraction cycle of a pure W tip; computational methods ([PDF](#))

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

Via our membership of the UK's HEC Materials Chemistry Consortium, which is funded by EPSRC (EP/L000202, EP/R029431), this work used both the ARCHER UK National Supercomputing Service (<http://www.archer.ac.uk>) and the UK Materials and Molecular Modelling Hub for computational resources, MMM Hub, which is partially funded by EPSRC (EP/P020194). This research was supported by the UK EPSRC Grant EP/N023587/1. H.S. acknowledges the support from the National Natural Science Foundation of China (Grant 21603086) and the China Scholarship Council (Grant 201608420186). J.M.R. thanks the Spanish MINECO and FICYT for financial support (Projects PGR2018-094814-B-C22 and FC-GRUPIN-IDI/2018/000177) and Universidad de Oviedo for a mobility grant to visit King's College London.

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