Supporting Information:

Atomic-Scale Patterning of Arsenic in Silicon by Scanning Tunneling Microscopy

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a) Kinetic Monte Carlo Simulations

Computer simulations of the evolution of an AsH$_3$-exposed Si(001) surface on time and length scales relevant to the STM experiments were conducted using the kinetic Monte Carlo (KMC) method$^1$ and a discrete lattice representation of the adsorbed molecular species. Key elements of this model are illustrated in Supplementary Figure S1.

The lattice used to represent the adsorbed species is shown in Figure S1 (a) with a unit cell (gray background shading) that corresponds to the (2x1) reconstruction of the Si(001) surface, and much larger super cells used in our simulations to represent an extended surface. Square boxes in Figure S1 (a) indicate discrete lattice sites that represent the surface binding sites for an AsH$_3$ molecule or any of its fragments. These sites come in three types, namely, dimer-end, end-bridge, and dimer-bridge, labeled ‘a’, ‘b’, and ‘c’ within the unit cell in Figure S1(a), respectively. Each of the sites exists in one of seven states, which indicates the type of molecular species occupying the site. The states used here are defined in Figure S1(b) and they represent AsH$_3$, AsH$_2$, AsH, As, and H molecular species, as well as a state F indicating a free or unoccupied site. Further defined is a distinct state X, which serves as a blocking state to indicate that a site is unavailable for occupation by another species. This is used in our model to block dimer-end sites when an adjacent dimer-bridge or end-bridge site is occupied, as such a bridging adsorbate would utilize the dangling bond valences at the two dimer ends involved in the bridge.

Together, the lattice and the configuration of states at all sites provides a compact representation of an extended Si(001) surface with a coverage of AsH$_3$ molecules in varying degrees of dissociation. An example configuration is shown in Fig. S1(c), describing a low-coverage surface with two AsH$_3$-related species, namely, a molecular AsH$_3$ molecular adsorbate at a dimer-end position near the top of the figure and a fully dissociated end-bridge As+3H species near the bottom.
Figure S1: KMC model of the Si(001) surface exposed to AsH₃. (a) The lattice representation of binding sites (indicated by squares) on the Si(001) surface with the unit cell shaded gray. (b) The set of seven possible occupation states at each binding site. (c) An example configuration in a 3x3 supercell featuring a molecular AsH₃ adsorbate and the end-bridge As+3H structure observed as the type-1 STM feature. (d,e) KMC transformations representing two types of chemisorption processes with the rate of transformation given by the pressure-dependent surface impingement rate. (f-o) KMC transformation representing various hydrogen-shift and rearrangement reactions relevant to AsH₃ dissociation on Si(001) with the rate of reaction defined using Arrhenius activation energies.
In a KMC simulation, a given initial configuration of states is advanced in time using a set of discrete transformations that occur with a defined rate\(^1\). In our case, the initial configuration is the bare surface without any adsorbates (i.e. all sites in the F state) and the set of transformations corresponds to a set of discrete chemical reactions that may occur upon \(\text{AsH}_3\) exposure, broadly divided into adsorption, dissociation, and rearrangement reactions. These transformations are set out in Figure S1(d) to (o), and they each comprise a pattern of specific states at a subset of lattice sites, a prescription for how these states change when the reaction occurs, and a parameter to define the rate of reaction. Note that an empty box in a transformation pattern indicates that the site can be in any state for the pattern to match.

For all other transformations [Figure S1 (f) to (o)] the rates are defined by an activation energy, which is converted into a rate constant using the Arrhenius equation with an assumed attempt frequency of \(10^{13}\) s\(^{-1}\) and a temperature of 298 K. The activation energies for most of the transformations are derived from the density functional theory calculations of suitable prototype reactions that represent the transformation. Here, these prototype reactions are those calculated for the main \(\text{AsH}_3\) dissociation pathway (cf. main text Fig. 1g) and some of the competing reaction pathways discussed in the main text. For other transformation which are indicated by an asterisk (\(\ast\)) in Fig. S1, the activation energies are derived by analogy to a similar reaction within the set. For example, the activation energy of the dimer-bridge \(\text{AsH} \rightarrow \text{As} + \text{H}\) transformation [Fig. S1(n)] assumed to be the same as that calculated by DFT for the end-bridge \(\text{AsH} \rightarrow \text{As} + \text{H}\) transformation [Fig. S1(n)].

One of the key tasks of a KMC simulation is to assemble a list of all possible transformations for a given configuration. This is accomplished by identifying all those transformation patterns that match the given configuration. Using again the example configuration in Fig. S1(c), the only transformation patterns that apply are the two types of adsorption reactions [Fig. S1(d) and (e)] matching many F-state sites in this configuration as well as the dissociation reactions [Fig. S1(f) and (g)] for the molecular \(\text{AsH}_3\) adsorbate near the top of Fig. S1(c). None of the transformation patterns match to the end-bridge \(\text{As} + 3\text{H}\) structure near the bottom of the figure, which reflects the fact that this structure represents an end point in the dissociation pathway of a single \(\text{AsH}_3\) molecule.
From the assembled list of all applicable transformations, a single transformation is selected at random and executed to advance the system to the next configuration, and the time is advanced also. A new list of applicable transformations is then assembled for the new configuration and the process repeats until the desired simulation time has been reached, or the system has reached a stable point where none of the transformations apply. Critically, both the random selection of the transformation and the time advancement are performed such that the all transformations occur at the specified rate when examined using in a sufficiently large ensemble average (see Gillespie, 1976 for details). The sequence of configurations that result from successive transformations applied in the course of a KMC simulation create a single trajectory in which AsH$_3$ molecules adsorb and dissociate in a stochastic manner. The pressure-dependent species coverages reported in the main text Fig. 2c using large 40x40 super cells and an average over 100 trajectories for each pressure, which sufficiently removes stochastic effects from the data.

All KMC simulations were carried out using a software developed by one of the authors (O.W.).
b) Hall and Magnetoresistance Measurements of As $\delta$-layers

Eight-terminal Hall bars were fabricated from multiple Si:As delta layer samples and electrically characterized by IV, Hall, and magnetoresistance measurements. The Hall bar geometry is illustrated below in Figure S2, alongside an example of a two-terminal IV measurement (terminals 8-4, sample d) demonstrating Ohmic contacting to the As delta layer.

![Figure S2: Eight-terminal Hall bar geometry and two-terminal IV measurement on a Si:As delta layer. a) The orientation of the perpendicular magnetic field $B_\perp$, and the measurement terminals for current and voltages $I_{xx}$, $V_{xx}$, and $V_{xy}$ are indicated on the Hall bar schematic. b) A two-terminal IV measurement (across terminals 8 and 4) on sample d (RTA = 500 °C) measured at 5 K, is both linear and symmetric indicating that the delta layer contacting is Ohmic.

Figure S3 shows Hall and magnetoresistance measurements for all six As delta-layer Hall bar samples along with fits to the data. The approach used in fitting to the weak-localisation data follows the methods of Sullivan et al., and assumes that the signal depends on both the magnitude and direction of the applied magnetic field, $B$, where the change in the conductance, $\delta \sigma_{xx}$, is for a weak spin-orbit donor. From the Hall and magnetoresistance measurements, $\Delta \sigma_{xx}$ is obtained from the measured resistivity $\rho_{xx}$:

$$\Delta \sigma_{xx}(B) = \frac{1}{\rho_{xx}(B)} - \frac{1}{\rho_{xx}(0)}. \quad (1)$$

For a perpendicular magnetic field, the change in conductance is:

$$\delta \sigma(B_\perp) = \left(\frac{e^2}{2\pi^2\hbar}\right) \left[ \Psi\left(\frac{1}{2} + \frac{\hbar}{4eB_\perp L_\phi^2}\right) - \Psi\left(\frac{1}{2} + \frac{\hbar}{2eB_\perp L^2}\right) + \ln\left(\frac{2L_\phi^2}{L^2}\right) \right]. \quad (2)$$

where $\Psi$ is the digamma function, $L_\phi$ the dephasing length and $L$ the mean free path.

For a parallel magnetic field, the change in conductance is:
\[ \delta \sigma(B_t) = \left( \frac{e^2}{2\pi^2 \hbar} \right) \ln(1 + \gamma B_t^2), \]

where \( \gamma \) is the fitting parameter.

Once the fits to the experimental weak-localisation data are determined, the fit parameters can be used to obtain an approximate measure of the \( \delta \)-layer thickness:

\[ T = \left( \frac{1}{4\pi} \right)^{1/4} \left( \frac{\hbar}{eL_\phi} \right)^2 \left( \frac{L}{L_c} \right)^{1/2} \gamma, \]

where \( L_c \) is the correlation length, assumed to be of the order of the mean donor spacing \( L_c = 1/\sqrt{n} \), where \( n \) is the carrier concentration extracted from the experimental Hall-measurements shown in the insets of Figure S3.

Figure S3: Summary of weak-localization data for parallel- (red) and perpendicular- (blue) magnetic fields. (a)-(d) The primary figures show the weak-localization data, whereas the insets show the Hall-measurements, with progressively increasing rapid thermal anneal (RTA) temperatures during the silicon overgrowth. The fits are applied from the equations provided in (Sullivan et al., 2004). No fit could be made to the parallel field data in (c).
Table S1 summarises values extracted from the Hall measurements ($n$, $\mu$, and $R_0$), and the best fit parameters for the weak-localization magnetoresistance plots for each of the arsenic $\delta$-layers grown using different rapid-thermal-anneal (RTA) temperatures. Using equations (1)-(3), a least-squares method is used to fit to the experimental weak-localisation data and the uncertainties in the fit parameters reflect the confidence intervals dictated by the fit parameters. For samples (a)-(b) and (d)-(e), there is a small feature present in the magnetoresistance near zero-field regime, which yields a negative change in conductance. Establishing the source of this behaviour in the Si:As system is beyond the scope of the current work and is the focus of ongoing investigations. For the purposes of the present work, all fits to extract thickness estimates were made by omitting the near zero-field behaviour, which is reflected in the uncertainties of the fit parameters shown in Table S1. For sample (c), no fits could be made to extract thickness estimates to the parallel field as the change in conductance is always negative.

<table>
<thead>
<tr>
<th>Sample</th>
<th>RTA ($^\circ$C)</th>
<th>Electron density ($n$) ($10^{14}$/cm$^2$)</th>
<th>Sheet Resistance ($R_0$) (10$^3$ Ω / □)</th>
<th>Mobility ($\mu$) (cm$^2$/V·s)</th>
<th>Mean free path ($L$) (nm)</th>
<th>Dephasing length ($L_\phi$) (nm)</th>
<th>Fitting Parameter ($\gamma$) ($10^{-4}$ T$^{-2}$)</th>
<th>Mean Thickness ($T$) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>250±15</td>
<td>1.15 ± 0.02</td>
<td>4.18 ± 0.02</td>
<td>13.0 ± 0.2</td>
<td>7.6 ± 0.2</td>
<td>30.9 ± 0.1</td>
<td>6.5 ± 0.4</td>
<td>0.8 ± 0.1</td>
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<tr>
<td>(b)</td>
<td>384±15</td>
<td>1.19 ± 0.07</td>
<td>2.49 ± 0.04</td>
<td>20.0 ± 1.3</td>
<td>8.1 ± 0.7</td>
<td>58.6 ± 0.6</td>
<td>27.0 ± 3.5</td>
<td>0.9 ± 0.1</td>
</tr>
<tr>
<td>(c)</td>
<td>438±15</td>
<td>1.29 ± 0.02</td>
<td>2.41 ± 0.02</td>
<td>20.0 ± 0.3</td>
<td>-</td>
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<tr>
<td>(d)</td>
<td>498±15</td>
<td>1.32 ± 0.01</td>
<td>1.69 ± 0.02</td>
<td>28.1 ± 0.2</td>
<td>7.1 ± 0.3</td>
<td>52.2 ± 0.2</td>
<td>75.0 ± 1.0</td>
<td>1.7 ± 0.1</td>
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<td>(e)</td>
<td>562±15</td>
<td>1.45 ± 0.10</td>
<td>1.54 ± 0.06</td>
<td>28.0 ± 2.0</td>
<td>16.0 ± 0.7</td>
<td>55.3 ± 0.8</td>
<td>67.0 ± 7.3</td>
<td>2.3 ± 0.2</td>
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</table>

*Table S1: As delta-layer electrical transport characteristics extracted from the magnetoresistance data shown in Figure S3. The electron density ($n$) and mobility ($\mu$) are determined from the fits to the inset data in Figure S3. The sheet resistance ($R_0$), mean-free path ($L$), dephasing length ($L_\phi$) and parallel field parameter ($\gamma$) are determined from the experimental fits to the primary data shown in Figure S3. The mean thickness ($T$) is then determined as in (Sullivan et al, 2004).*

**Supporting Information References**
