Electronic Supplementary Information (ESI) for:

Classification of epitaxy in reciprocal and real space: rigid *versus* flexible lattices

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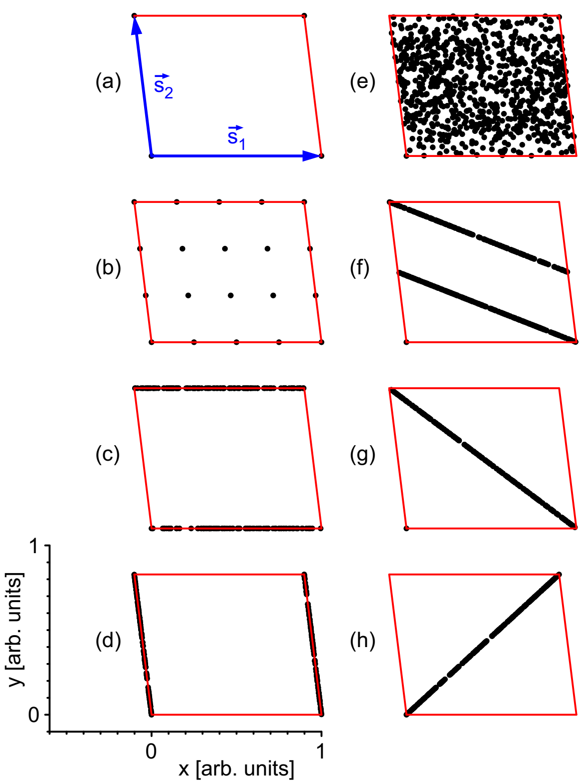
ESI 1 The projection method for an oblique substrate lattice

For the sake of completeness we demonstrate here that the projection of real-space adsorbate lattice points onto a substrate unit cell (put forward in section 2.5 of the main text) is naturally not restricted to any special Bravais lattice type. Indeed, no prerequisite other than linear independence was made for $\vec{s}_1$ and $\vec{s}_2$ in the first place; but because Fig. 1 in the main text was drawn for $|\vec{s}_1| = |\vec{s}_2|$ and $\measuredangle(\vec{s}_1, \vec{s}_2) = 120°$ one might have gotten the impression that our arguments would have been valid for hexagonal substrates only. This is clearly not the case as depicted in Supp. Fig. 1 for an arbitrary oblique substrate lattice, *i.e.*, $|\vec{s}_1| \neq |\vec{s}_2|$ and $\measuredangle(\vec{s}_1, \vec{s}_2) \neq 90°$. There, $|\vec{s}_2| = G \cdot |\vec{s}_1|$ is chosen as an example, with $G = \frac{2}{\pi}\int_0^1 \frac{dx}{\sqrt{1-x^4}} = 0.8346268\ldots$ being Gauss's constant.



Supp. Fig. 1 Projections of real-space adsorbate lattice points (•) onto a substrate unit cell by calculating $(p \cdot \vec{a}_1 + q \cdot \vec{a}_2) - (m \cdot \vec{s}_1 + n \cdot \vec{s}_2)$ numerically, with $p, q \in \mathbb{Z}$ chosen randomly between -1000 and 1000, and setting $m, n \in \mathbb{Z}$ appropriately. The substrate unit cell drawn in red is spanned by the basis vectors $\vec{s}_1$ and $\vec{s}_2$ whose lengths are $|\vec{s}_1| = 1$ and $|\vec{s}_2| = G$, while $\measuredangle(\vec{s}_1, \vec{s}_2) = 97°$. Note that this choice is arbitrary, and any other substrate unit cell will yield similar images. The following epitaxy matrices from Table 1 of the main text are used: (a) $\mathbf{M}_\mathrm{A}$, (b) $\mathbf{M}_\mathrm{B}$, (c) $\mathbf{M}_\mathrm{C}$, (d) $\mathbf{M}_\mathrm{D}$, (e) $\mathbf{M}_\mathrm{F}$ [similar results for $\mathbf{M}_\mathrm{G}$], (f) $\mathbf{M}_\mathrm{H}$ [similar results for $\mathbf{M}_\mathrm{E}$], (g) $\mathbf{M}_\mathrm{I}$, (h) $\mathbf{M}_\mathrm{J}$.

Apart from the different substrate unit cell, these projection patterns were numerically calculated in exactly the same way as described in section 2.5 using the exemplary epitaxy matrices from Table 1 in the main text. Note that we did not simply shear the projection patterns of the hexagonal substrate but performed independent calculations for all patterns.

ESI 2 Permutation of basis vectors

Permutation of the basis vectors $\vec{b}_1 = \vec{a}_2$ and $\vec{b}_2 = \vec{a}_1$ is realized by

$$\begin{pmatrix} \vec{b}_1 \\ \vec{b}_2 \end{pmatrix} = \mathbf{B}_\mathrm{P} \cdot \begin{pmatrix} \vec{a}_1 \\ \vec{a}_2 \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \cdot \begin{pmatrix} \vec{a}_1 \\ \vec{a}_2 \end{pmatrix} \qquad \text{(S1)}$$

Several important conclusions can be drawn:

(a) The basis transformation in eqn (S1) does not change the area of the parallelogram spanned by the basis vectors. It can easily be seen that $|\vec{b}_1 \times \vec{b}_2| = |\vec{a}_1 \times \vec{a}_2|$ since $\det(\mathbf{B}_\mathrm{P}) = -1$. The minus sign herein means that the handedness of the set of basis vectors is changed. Although right-handed coordinate systems are generally preferred by convention, left-handed coordinate systems are in principle equally possible and do not render any of the arguments here invalid.

(b) For any basis transformation $\mathbf{B}$ with $|\det(\mathbf{B})| = 1$ it follows that if $\vec{a}_1$ and $\vec{a}_2$ are primitive basis vectors, then $\vec{b}_1$ and $\vec{b}_2$ are also primitive basis vectors.

(c) Permutation of the basis vectors of the substrate simply permutes the columns of the epitaxy matrix.

$$\begin{pmatrix} \vec{a}_1 \\ \vec{a}_2 \end{pmatrix} = \begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} \cdot \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \cdot \begin{pmatrix} \vec{s}_1 \\ \vec{s}_2 \end{pmatrix} = \begin{pmatrix} M_{12} & M_{11} \\ M_{22} & M_{21} \end{pmatrix} \cdot \begin{pmatrix} \vec{s}_1 \\ \vec{s}_2 \end{pmatrix} \qquad \text{(S2)}$$

Therefore, arguments applied to a specific column of the epitaxy matrix do not constitute a loss of generality.

(d) Permutation of the basis vectors of the adsorbate simply permutes the rows of the epitaxy matrix.

$$\begin{pmatrix} \vec{b}_1 \\ \vec{b}_2 \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \cdot \begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} \cdot \begin{pmatrix} \vec{s}_1 \\ \vec{s}_2 \end{pmatrix} = \begin{pmatrix} M_{21} & M_{22} \\ M_{11} & M_{12} \end{pmatrix} \cdot \begin{pmatrix} \vec{s}_1 \\ \vec{s}_2 \end{pmatrix} \qquad \text{(S3)}$$

Therefore, arguments applied to a specific row of the epitaxy matrix do not constitute a loss of generality.

ESI 3 Choice of basis vectors and change of basis

Let $\vec{s}_1$ and $\vec{s}_2$ be the basis vectors of a two-dimensional grid of lattice points with strict translational symmetry. We may define an alternative set of basis vectors $\tilde{\vec{s}}_1$ and $\tilde{\vec{s}}_2$ according to:

$$\begin{pmatrix} \vec{s}_1 \\ \vec{s}_2 \end{pmatrix} = \begin{pmatrix} a & b \\ c & d \end{pmatrix} \cdot \begin{pmatrix} \tilde{\vec{s}}_1 \\ \tilde{\vec{s}}_2 \end{pmatrix} \quad (a, b, c, d \in \mathbb{Z}) \qquad \text{(S4)}$$

Since linear independence of $\vec{s}_1$ and $\vec{s}_2$ is a prerequisite for a set of basis vectors, it follows that $\tilde{\vec{s}}_1$ and $\tilde{\vec{s}}_2$ are also linearly independent provided that $\det\left(\begin{smallmatrix} a & b \\ c & d \end{smallmatrix}\right) \neq 0$. If $a,b,c,d \in \mathbb{Z}$ and if $\det\left(\begin{smallmatrix} a & b \\ c & d \end{smallmatrix}\right) = 1$ then both bases describe the same set of lattice points, *i.e.*, the position vectors of all lattice points can be expressed as linear combinations of the respective basis vectors with integer coefficients. An epitaxial relation as in eqn (1) would then read

$$\begin{pmatrix} \vec{a}_1 \\ \vec{a}_2 \end{pmatrix} = \underbrace{\begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} \cdot \begin{pmatrix} a & b \\ c & d \end{pmatrix}}_{\tilde{\mathbf{M}}} \cdot \begin{pmatrix} \tilde{\vec{s}}_1 \\ \tilde{\vec{s}}_2 \end{pmatrix} \tag{S5}$$

Owing to the freedom of choice for the basis vectors it is clear that the transformation of the basis cannot change the fundamental nature of epitaxial coincidences. Only their indices should obviously be modified since eqn (7) would now read

$$\begin{pmatrix} h_\mathrm{a} \\ k_\mathrm{a} \end{pmatrix} = \underbrace{\begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} \cdot \begin{pmatrix} a & b \\ c & d \end{pmatrix}}_{\tilde{\mathbf{M}}} \cdot \begin{pmatrix} \tilde{h}_\mathrm{s} \\ \tilde{k}_\mathrm{s} \end{pmatrix} \tag{S6}$$

In particular, if we restrict ourselves to basis transformations with

$$\det \begin{pmatrix} a & b \\ c & d \end{pmatrix} = a \cdot d - b \cdot c = 1 \quad (a,b,c,d \in \mathbb{Z}) \tag{S7}$$

then this should not influence the specific type of epitaxy (*i.e.*, commensurism, HOC, POL, LOL) at all. In the case of an arbitrary coincidence of the order $(h_\mathrm{s}, k_\mathrm{s})$ one can try to transform the basis, such that (without loss of generality) the order of coincidence with the new basis is $(\tilde{h}_\mathrm{s}, \tilde{k}_\mathrm{s}) = (1,0)$ and therefore primitive:

$$\begin{pmatrix} h_\mathrm{s} \\ k_\mathrm{s} \end{pmatrix} = \begin{pmatrix} a & b \\ c & d \end{pmatrix} \cdot \begin{pmatrix} \tilde{h}_\mathrm{s} \\ \tilde{k}_\mathrm{s} \end{pmatrix} \overset{!}{=} \begin{pmatrix} a & b \\ c & d \end{pmatrix} \cdot \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} a \\ c \end{pmatrix}$$

In combination with eqn (S7) this will lead to integer solutions for b and d with

$$h_\mathrm{s} \cdot d - b \cdot k_\mathrm{s} = 1 \tag{S8}$$

<u>unless</u> $h_\mathrm{s} = n \cdot p$ and $k_\mathrm{s} = n \cdot q$ (with $n,p,q \in \mathbb{Z}$ and $|n| \geq 2$), because this yields $h_\mathrm{s} \cdot d - b \cdot k_\mathrm{s} = n \cdot (p \cdot d - b \cdot q) \neq 1$ in violation of eqn (S8). Note that this condition includes $(h_\mathrm{s}, k_\mathrm{s}) = (0,0)$, $(2,0)$, $(2,2)$, $(3,0)$, $(3,3)$, $(4,0)$, $(4,2)$, and so on, *i.e.*, non-Miller indices.

If the order of coincidence $(h_\mathrm{s}, k_\mathrm{s})$ does not contain a common factor n with $|n| \geq 2$, a possible change of basis is described by the matrix

$$\begin{pmatrix} a & b \\ c & d \end{pmatrix} = \begin{pmatrix} h_\mathrm{s} & b \\ k_\mathrm{s} & (1 + b \cdot k_\mathrm{s})/h_\mathrm{s} \end{pmatrix} \tag{S9}$$

To provide an example, we consider a coincidence of the order $(h_\mathrm{s}, k_\mathrm{s}) = (3,2)$ and choose the basis transformation

$$\begin{pmatrix} \vec{s}_1 \\ \vec{s}_2 \end{pmatrix} = \begin{pmatrix} 3 & 4 \\ 2 & 3 \end{pmatrix} \cdot \begin{pmatrix} \tilde{\vec{s}}_1 \\ \tilde{\vec{s}}_2 \end{pmatrix} \tag{S10}$$

It is straightforward to verify that

$$\begin{pmatrix} h_\mathrm{s} \\ k_\mathrm{s} \end{pmatrix} = \begin{pmatrix} 3 & 4 \\ 2 & 3 \end{pmatrix} \cdot \begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{S11}$$

and that $\det\left(\begin{smallmatrix} 3 & 4 \\ 2 & 3 \end{smallmatrix}\right) = 1$. Therefore, this basis transformation is not only allowed, it also leaves the unit cell spanned by $\tilde{\vec{s}}_1$ and $\tilde{\vec{s}}_2$ primitive provided that $\vec{s}_1$ and $\vec{s}_2$ are primitive in the first place. This example illustrates that for the basis vectors $\vec{s}_1$ and $\vec{s}_2$ the coincidence $(h_\mathrm{s}, k_\mathrm{s}) = (3,2)$ is non-primitive (which would be LOL according to previous classifications[4,19]), while for the basis vectors $\tilde{\vec{s}}_1$ and $\tilde{\vec{s}}_2$ the corresponding coincidence $(\tilde{h}_\mathrm{s}, \tilde{k}_\mathrm{s}) = (1,0)$ is primitive (which would be POL according to previous classifications[4,19]). In such cases a discrimination between POL and LOL does depend on the choice of the basis which is not meaningful.

On the other hand, we consider a coincidence of the order $(h_\mathrm{s}, k_\mathrm{s}) = (4,2)$ and the basis transformation

$$\begin{pmatrix} \vec{s}_1 \\ \vec{s}_2 \end{pmatrix} = \begin{pmatrix} 4 & b \\ 2 & d \end{pmatrix} \cdot \begin{pmatrix} \tilde{\vec{s}}_1 \\ \tilde{\vec{s}}_2 \end{pmatrix} \tag{S12}$$

Again, it is straightforward to verify that

$$\begin{pmatrix} h_\mathrm{s} \\ k_\mathrm{s} \end{pmatrix} = \begin{pmatrix} 4 & b \\ 2 & d \end{pmatrix} \cdot \begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{S13}$$

However, $\det\left(\begin{smallmatrix} 4 & b \\ 2 & d \end{smallmatrix}\right) \neq 1$ for all $b,d \in \mathbb{Z}$. In such cases, a primitive order of coincidence $(\tilde{h}_\mathrm{s}, \tilde{k}_\mathrm{s}) = (1,0)$ can only be achieved for $|\det\left(\begin{smallmatrix} 4 & b \\ 2 & d \end{smallmatrix}\right)| \geq 2$ meaning that $\tilde{\vec{s}}_1$ and $\tilde{\vec{s}}_2$ would never be primitive even if $\vec{s}_1$ and $\vec{s}_2$ are. If h_s and k_s have a common divisor $|n| \geq 2$, then a discrimination between POL and LOL would in principle be possible. Nevertheless, as already stated in the main text, it becomes evident that a strict distinction between POL and LOL – *via* the order of coincidence $(h_\mathrm{s}, k_\mathrm{s})$ being either primitive or non-primitive – may be rather cumbersome owing to the freedom of choice of basis vectors. We thus recommend to employ the term **"on-line" coincident (OLC) of the order $(h_\mathrm{s}, k_\mathrm{s})$** and of course to specify the basis vectors chosen to describe the respective lattices in order to prevent ambiguity.

ESI 4 Distinction of cases

A classification scheme for lattice epitaxy can be derived from eqn (7) by splitting each epitaxy matrix element M_{ij} into a rational ($R_{ij} \in \mathbb{Q}$) and an irrational ($I_{ij} \in \mathbb{R} \backslash \mathbb{Q}$) part: $M_{ij} = R_{ij} + I_{ij}$. Here, we use the fact that the sum of a rational and an irrational number is irrational. Consequently, we can include any desired irrational number in our discussion of $\mathbf{M}$, but also all rational numbers can be considered by simply omitting the respective I_{ij}. We recall here that an epitaxy matrix $\mathbf{M}$ containing at least one irrational element is incompatible with commensurism or higher order commensurism, *cf.* section 2.4. Therefore, such an epitaxy matrix either describes an "on-line" registry (*i.e.*, all coincidences are linearly dependent) or incommensurism (*i.e.*, no coincidence at all). In the following we develop a complete account of all possible cases of $\mathbf{M}$ with at least one irrational element. The discussion is based on eqn (7) rewritten as

$$\begin{pmatrix} h_\mathrm{a} \\ k_\mathrm{a} \end{pmatrix} = \begin{pmatrix} R_{11} + I_{11} & R_{12} + I_{12} \\ R_{21} + I_{21} & R_{22} + I_{22} \end{pmatrix} \cdot \begin{pmatrix} h_\mathrm{s} \\ k_\mathrm{s} \end{pmatrix} \tag{S14}$$

ESI 4.1 Two irrational elements on a diagonal and at least one rational element.

For $M_{12}, M_{21} \in \mathbb{R}\backslash\mathbb{Q}$ and [without loss of generality] for $M_{11} \in \mathbb{Q}$ eqn (14) in the main text can only be fulfilled for $k_s = 0$. This yields immediately $k_a = M_{21} \cdot h_s$ (for any $M_{22} \in \mathbb{R}$) which cannot be solved since M_{21} was assumed irrational. Hence, there are no integer solutions $\{h_a, k_a, h_s, k_s\} \neq 0$ to eqn (14) for the cases $\begin{pmatrix} \mathbb{Q} & \mathbb{R}\backslash\mathbb{Q} \\ \mathbb{R}\backslash\mathbb{Q} & \mathbb{R}\backslash\mathbb{Q} \end{pmatrix}$ and $\begin{pmatrix} \mathbb{Q} & \mathbb{R}\backslash\mathbb{Q} \\ \mathbb{R}\backslash\mathbb{Q} & \mathbb{Q} \end{pmatrix}$ as well as all permutations of rows and columns thereof.

ESI 4.2 Two rational elements: one rational and one irrational row.

For $M_{11}, M_{12} \in \mathbb{R}\backslash\mathbb{Q}$ and for $M_{21}, M_{22} \in \mathbb{Q}$ eqn (S14) yields

$$h_a = (R_{11} + I_{11}) \cdot h_s + (R_{12} + I_{12}) \cdot k_s \tag{S15}$$

$$k_a = R_{21} \cdot h_s + R_{22} \cdot k_s \tag{S16}$$

which can only be solved if $I_{11} \cdot h_s + I_{12} \cdot k_s = 0$, otherwise the rationality of all R_{ij} and the irrationality of all I_{ij} would not allow the right-hand side of eqn (S15) to become integer. Consequently:

$$h_a = \underbrace{(R_{11} - R_{12} \cdot I_{11}/I_{12})}_{\in\mathbb{Q}} \cdot h_s = \underbrace{(R_{12} - R_{11} \cdot I_{12}/I_{11})}_{\in\mathbb{Q}} \cdot k_s \tag{S17}$$

$$k_a = \underbrace{(R_{21} - R_{22} \cdot I_{11}/I_{12})}_{\in\mathbb{Q}} \cdot h_s = \underbrace{(R_{22} - R_{21} \cdot I_{12}/I_{11})}_{\in\mathbb{Q}} \cdot k_s \tag{S18}$$

Only under the condition that $I_{11}/I_{12} = -k_s/h_s \in \mathbb{Q}$ this yields an "on-line" registry. However, in this particular case a coincidence cannot be primitive, *i.e.*, $(h_s, k_s) = (1,0)$ or $(h_s, k_s) = (0,1)$ and multiples thereof can be ruled out here. If either $h_s = 0$ or $k_s = 0$ then it follows immediately from eqns (S17) and (S18) that $h_a = 0$ and simultaneously $k_a = 0$, which gives the trivial equality $\vec{G}_a(0,0) = \vec{G}_s(0,0) = \vec{0}$ and does not constitute a coincidence. Hence, there are integer solutions $\{h_a, k_a, h_s, k_s\} \neq 0$ to eqn (14) for the case $\begin{pmatrix} \mathbb{R}\backslash\mathbb{Q} & \mathbb{R}\backslash\mathbb{Q} \\ \mathbb{Q} & \mathbb{Q} \end{pmatrix}$ if $I_{11} \cdot h_s = -I_{12} \cdot k_s$ and, likewise, for the case $\begin{pmatrix} \mathbb{Q} & \mathbb{Q} \\ \mathbb{R}\backslash\mathbb{Q} & \mathbb{R}\backslash\mathbb{Q} \end{pmatrix}$ if $I_{21} \cdot h_s = -I_{22} \cdot k_s$.

ESI 4.3 Two rational elements in a column and at least one irrational element.

For $M_{11}, M_{21} \in \mathbb{Q}$ and [without loss of generality] for $M_{12} \in \mathbb{R}\backslash\mathbb{Q}$ eqn (14) can only be fulfilled for $k_s = 0$. What remains is then

$$h_a = M_{11} \cdot h_s \quad \text{and} \quad k_a = M_{21} \cdot h_s \tag{S19}$$

This is consistent with the initial assumption of two rational elements in a column (here: the first). Therefore, in this case there is always an "on-line" registry with $h_s \neq 0$, irrespective of the fourth epitaxy matrix element $M_{22} \in \mathbb{R}$ (recall that the trivial equality $\vec{G}_a(0,0) = \vec{G}_s(0,0) = \vec{0}$ is not counted as a coincidence). In other words, there are always integer solutions $\{h_a, k_a, h_s, k_s\} \neq 0$ to eqn (14) for the cases $\begin{pmatrix} \mathbb{Q} & \mathbb{R}\backslash\mathbb{Q} \\ \mathbb{Q} & \mathbb{Q} \end{pmatrix}$ and $\begin{pmatrix} \mathbb{Q} & \mathbb{R}\backslash\mathbb{Q} \\ \mathbb{Q} & \mathbb{R}\backslash\mathbb{Q} \end{pmatrix}$ as well as all permutations of rows and columns thereof.

A noteworthy special case occurs for $M_{11}, M_{21} \in \mathbb{Z}$ and [without loss of generality] for $M_{12} \in \mathbb{R}\backslash\mathbb{Q}$. Then eqn (7) is fulfilled by

$$\begin{pmatrix} h_a \\ k_a \end{pmatrix} = \begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} \cdot \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} M_{11} \\ M_{21} \end{pmatrix} \tag{S20}$$

which is tantamount to $\vec{G}_a(M_{11}, M_{21}) = \vec{G}_s(1,0)$. In other words, if the first [second] column of the epitaxy matrix consists of integer elements only, then there is always a coincidence with the *primitive* reciprocal lattice vector of the substrate $\vec{s}_1^*$ [$\vec{s}_2^*$]. This corresponds to the definition of point-on-line (POL) coincidences.[4,19]

Nonetheless, we emphasize that a column consisting of integer elements only is *not* mandatory for a POL registry. We turn back to section ESI 3 and discuss two frequent special cases. First, let us consider a particular change of the substrate basis according to eqn (S5)

$$\begin{pmatrix} \vec{a}_1 \\ \vec{a}_2 \end{pmatrix} = \underbrace{\begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} \cdot \begin{pmatrix} 1 & 0 \\ f & 1 \end{pmatrix}}_{\tilde{\mathbf{M}}} \cdot \begin{pmatrix} \tilde{\vec{s}}_1 \\ \tilde{\vec{s}}_2 \end{pmatrix} \tag{S21}$$

with $f \in \mathbb{Z}$ with $f \neq 0$. We are still interested in the special case $M_{11}, M_{21} \in \mathbb{Z}$ and [without loss of generality] $M_{12} \in \mathbb{R}\backslash\mathbb{Q}$, because this leads to a coincidence with the *primitive* reciprocal lattice vector of the substrate $\vec{s}_1^*$, thus expressing a POL coincidence with $(h_s, k_s) = (1,0)$ in the first place. Upon changing the substrate basis, the transformed epitaxy matrix $\tilde{\mathbf{M}}$ is obtained through:

$$\tilde{\mathbf{M}} = \begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} \cdot \begin{pmatrix} 1 & 0 \\ f & 1 \end{pmatrix}$$

$$= \begin{pmatrix} (M_{11} + f \cdot M_{12}) & M_{12} \\ (M_{21} + f \cdot M_{22}) & M_{22} \end{pmatrix} = \begin{pmatrix} \tilde{M}_{11} & \tilde{M}_{12} \\ \tilde{M}_{21} & \tilde{M}_{22} \end{pmatrix} \tag{S22}$$

Quite importantly, both elements of the first row of $\tilde{\mathbf{M}}$ are irrational. An obvious consequence is that $\tilde{\mathbf{M}}$ does not contain a column with integer elements only. Still, $\tilde{\mathbf{M}}$ describes a POL coincidence since the type of epitaxy should not change upon a legitimate basis transformation. It is clear that the order of coincidence $(\tilde{h}_s, \tilde{k}_s)$ has changed upon transforming the basis according to:

$$\begin{pmatrix} h_s \\ k_s \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ f & 1 \end{pmatrix} \cdot \begin{pmatrix} \tilde{h}_s \\ \tilde{k}_s \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{S23}$$

$$\begin{pmatrix} \tilde{h}_s \\ \tilde{k}_s \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ -f & 1 \end{pmatrix} \cdot \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 1 \\ -f \end{pmatrix} \tag{S24}$$

We see that for $f = -1$ the order of coincidence is $(\tilde{h}_s, \tilde{k}_s) = (1,1)$ and that the *summation of the elements of each row* of $\tilde{\mathbf{M}}$ [*cf.* eqn (S22)] yields integer values. Similarly, for $f = 1$ the order of coincidence is $(\tilde{h}_s, \tilde{k}_s) = (1,-1)$ and the *subtraction of the elements of each row* of $\tilde{\mathbf{M}}$ yields integer values. These two special cases occur quite frequently.[33] It is important to realize that the summation rule and the subtraction rule have nothing to do with the type of Bravais lattice of the substrate, since no restrictions other than linear independence apply to $\vec{s}_1$ and $\vec{s}_2$ in any of the above arguments. Especially, a hexagonal symmetry is *not* required for these rules as stated in previous work.[1]

ESI 4.4 Four irrational elements.

Eqn (S14) is satisfied if all of the following conditions are met:

$$I_{11} \cdot h_\mathrm{s} = -I_{12} \cdot k_\mathrm{s} \tag{S25}$$

$$I_{21} \cdot h_\mathrm{s} = -I_{22} \cdot k_\mathrm{s} \tag{S26}$$

$$h_\mathrm{a} = R_{11} \cdot h_\mathrm{s} + R_{12} \cdot k_\mathrm{s} \tag{S27}$$

$$k_\mathrm{a} = R_{21} \cdot h_\mathrm{s} + R_{22} \cdot k_\mathrm{s} \tag{S28}$$

Under these circumstances there exists a coincidence. This is remarkable because in the case of a fully irrational epitaxy matrix it is obvious that no real-space matching of lattice points whatsoever can be achieved even for infinitely large grids (with translational symmetry).

ESI 5 Further comments and derivations

The derivation of eqn (18) of the main text is shown explicitly in eqn (S29). Further, we demonstrate in eqn (S30) that for a given coincidence $\vec{G}_\mathrm{a}(h_\mathrm{a}, k_\mathrm{a}) = \vec{G}_\mathrm{s}(h_\mathrm{s}, k_\mathrm{s})$ the lattice direction of the adsorbate $[-k_\mathrm{a} \cdot \vec{a}_1 + h_\mathrm{a} \cdot \vec{a}_2]$ is parallel to that of the substrate $[-k_\mathrm{s} \cdot \vec{s}_1 + h_\mathrm{s} \cdot \vec{s}_2]$, which illustrates the nomenclature "line-on-line". As stated in the main text it is clear that this very coincidence also implies equidistant lines, *i.e.*, $d_{h_\mathrm{a},k_\mathrm{a}} = d_{h_\mathrm{s},k_\mathrm{s}}$.

$$\begin{aligned}
(p \cdot \vec{a}_1 + q \cdot \vec{a}_2) - (m \cdot \vec{s}_1 + n \cdot \vec{s}_2) &= (p \cdot M_{11} + q \cdot M_{21} - m) \cdot \vec{s}_1 + (p \cdot M_{12} + q \cdot M_{22} - n) \cdot \vec{s}_2 \\
&= \left(p \cdot \frac{h_\mathrm{a} - M_{12} \cdot k_\mathrm{s}}{h_\mathrm{s}} + q \cdot M_{21} - m\right) \cdot \vec{s}_1 + \left(p \cdot M_{12} + q \cdot \frac{k_\mathrm{a} - M_{21} \cdot h_\mathrm{s}}{k_\mathrm{s}} - n\right) \cdot \vec{s}_2 \\
&= \left(p \cdot \frac{h_\mathrm{a}}{h_\mathrm{s}} - m\right) \cdot \vec{s}_1 + \left(q \cdot \frac{k_\mathrm{a}}{k_\mathrm{s}} - n\right) \cdot \vec{s}_2 + \left(-p \cdot M_{12} \cdot \frac{k_\mathrm{s}}{h_\mathrm{s}} + q \cdot M_{21}\right) \cdot \vec{s}_1 + \left(p \cdot M_{12} - q \cdot M_{21} \cdot \frac{h_\mathrm{s}}{k_\mathrm{s}}\right) \cdot \vec{s}_2 \\
&= \left(p \cdot \frac{h_\mathrm{a}}{h_\mathrm{s}} - m\right) \cdot \vec{s}_1 + \left(q \cdot \frac{k_\mathrm{a}}{k_\mathrm{s}} - n\right) \cdot \vec{s}_2 + \left(\frac{p \cdot M_{12}}{h_\mathrm{s}} - \frac{q \cdot M_{21}}{k_\mathrm{s}}\right) \cdot [-k_\mathrm{s} \cdot \vec{s}_1 + h_\mathrm{s} \cdot \vec{s}_2]
\end{aligned} \tag{S29}$$

$$\begin{aligned}
-k_\mathrm{a} \cdot \vec{a}_1 + h_\mathrm{a} \cdot \vec{a}_2 &= -(M_{21} \cdot h_\mathrm{s} + M_{22} \cdot k_\mathrm{s}) \cdot [M_{11} \cdot \vec{s}_1 + M_{12} \cdot \vec{s}_2] + (M_{11} \cdot h_\mathrm{s} + M_{12} \cdot k_\mathrm{s}) \cdot [M_{21} \cdot \vec{s}_1 + M_{22} \cdot \vec{s}_2] \\
&= [h_\mathrm{s} M_{11}(M_{21} - M_{21}) - k_\mathrm{s}(M_{22} M_{11} - M_{12} M_{21})] \cdot \vec{s}_1 + [k_\mathrm{s} M_{22}(M_{12} - M_{12}) + h_\mathrm{s}(M_{22} M_{11} - M_{12} M_{21})] \cdot \vec{s}_2 \\
&= (M_{22} M_{11} - M_{12} M_{21}) \cdot [-k_\mathrm{s} \cdot \vec{s}_1 + h_\mathrm{s} \cdot \vec{s}_2] = \det \mathbf{M} \cdot [-k_\mathrm{s} \cdot \vec{s}_1 + h_\mathrm{s} \cdot \vec{s}_2] \quad \Rightarrow \underline{\underline{[-k_\mathrm{a} \cdot \vec{a}_1 + h_\mathrm{a} \cdot \vec{a}_2] \parallel [-k_\mathrm{s} \cdot \vec{s}_1 + h_\mathrm{s} \cdot \vec{s}_2]}}
\end{aligned} \tag{S30}$$

End of file.