Real Surfaces

M. Ceriotti - MX304

EPFL

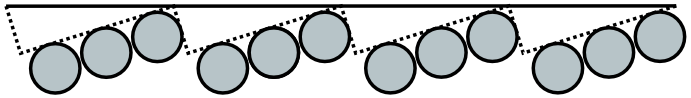
Outline

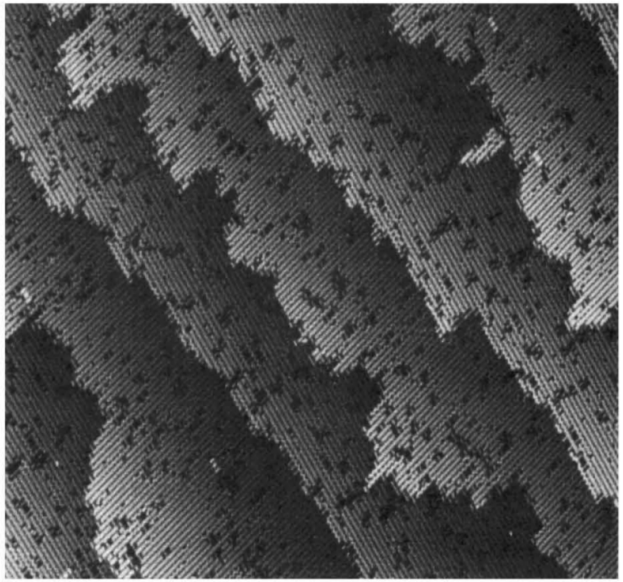
- Defects at surfaces
- Terraces, ledges, kinks
- Concentration of adatoms and vacancies, roughening
- Surface reconstructions and relaxation

Singular Surfaces and Faceting

- Surfaces that correspond to cusps in the Wulff plot are very stable, and atomically flat (“singular surfaces”)
- Surfaces that are slightly tilted (“vicinal surfaces”) exhibit faceting: flat, singular-orientation **terraces** separated by **ledges**
- Surface energy can be worked out as a function of the angle θ

$$\gamma_{sv}(\theta) = \gamma_0 \cos\theta + \frac{\eta E_l}{h_l} \sin\theta$$

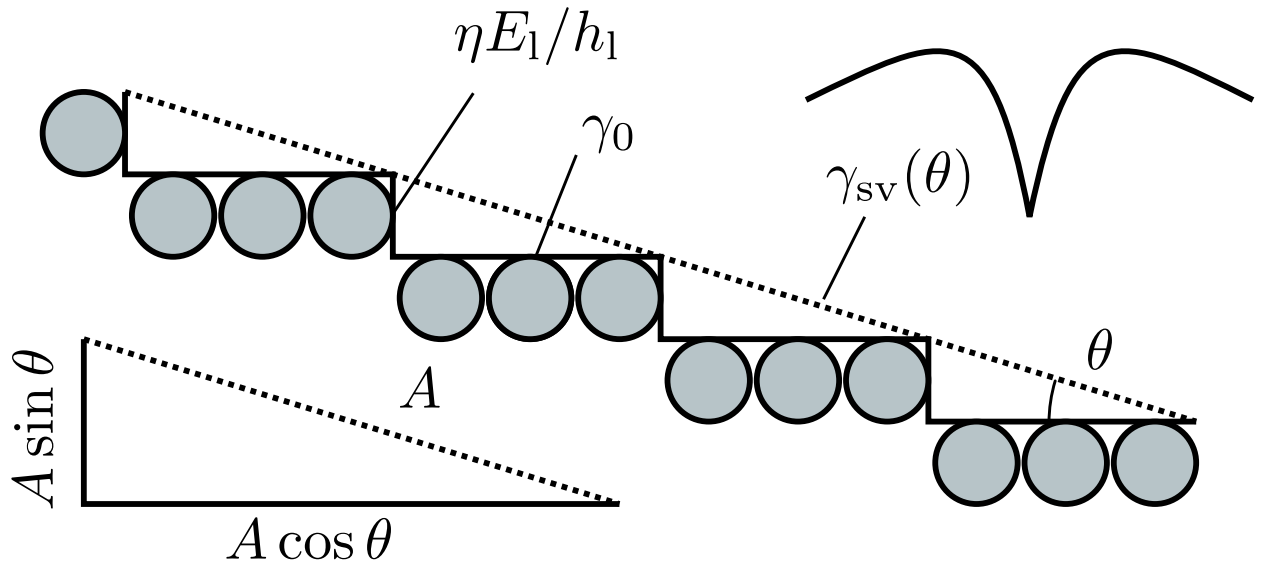




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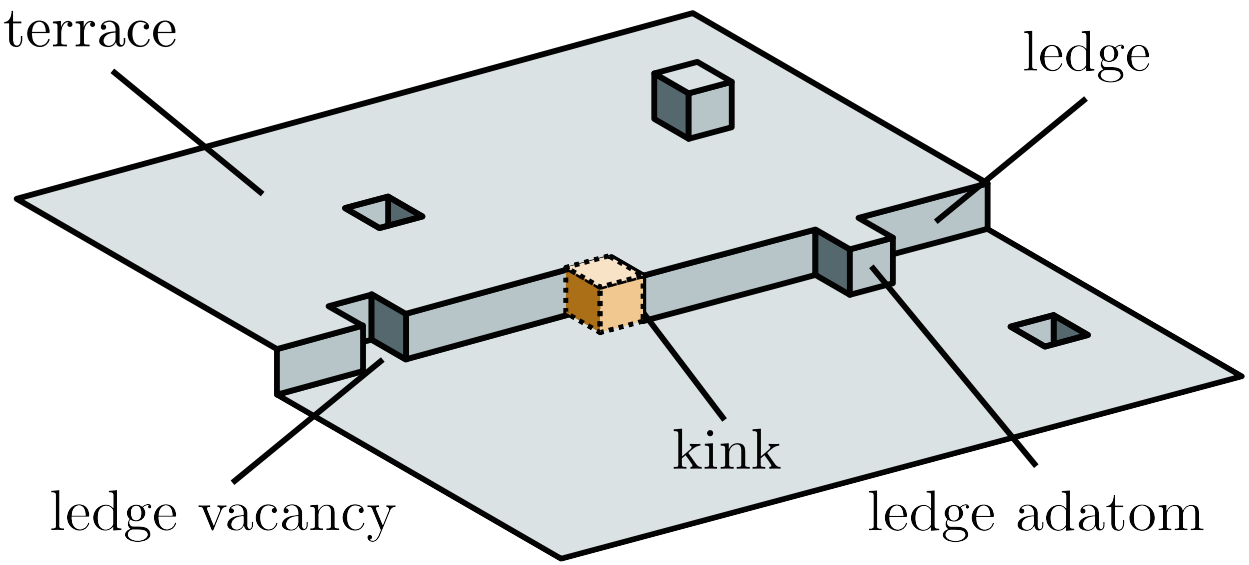
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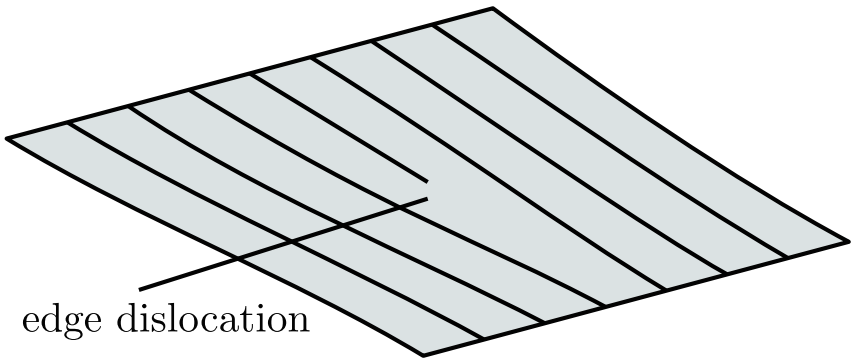
Surface Defects

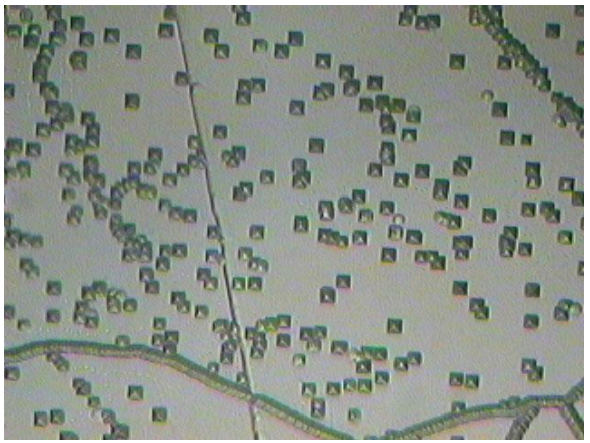
- A surface can have point defects just as a solid crystal can (vacancies, adatoms)
- In a real case, with ledges and kinks, the story is more complex
- Kinks are special, in that you can add an atom without changing the number of broken bonds



Bulk Defects at Surfaces

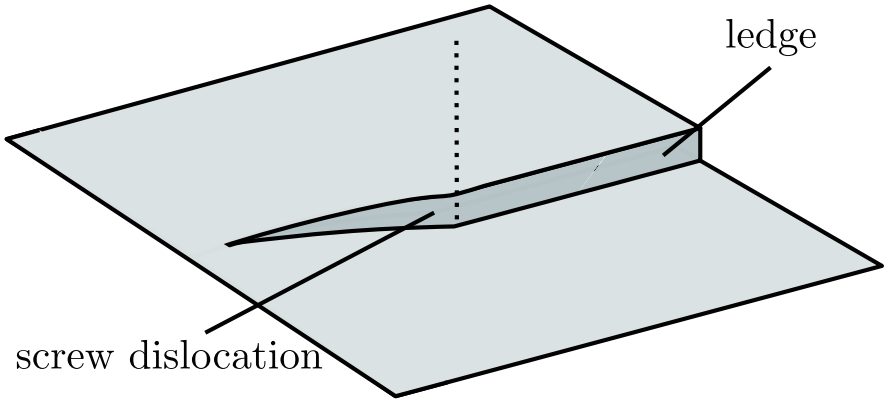
- Surfaces contain *kinetic* defects, that are typically connected to bulk defects (grain boundaries, dislocations)
- Surfacing dislocations can be seen by etching, or by decoration of the surface
- Screw dislocations can be a mechanism for crystal growth

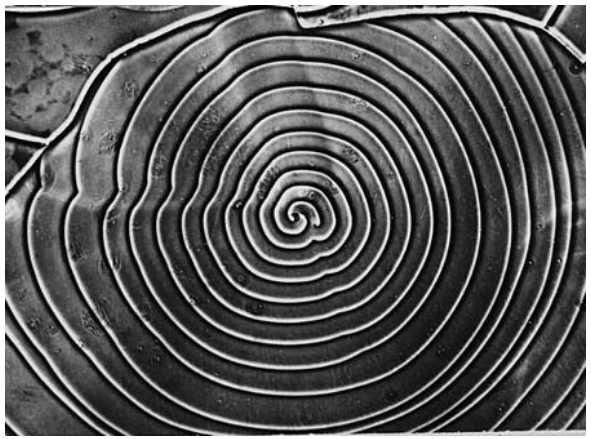




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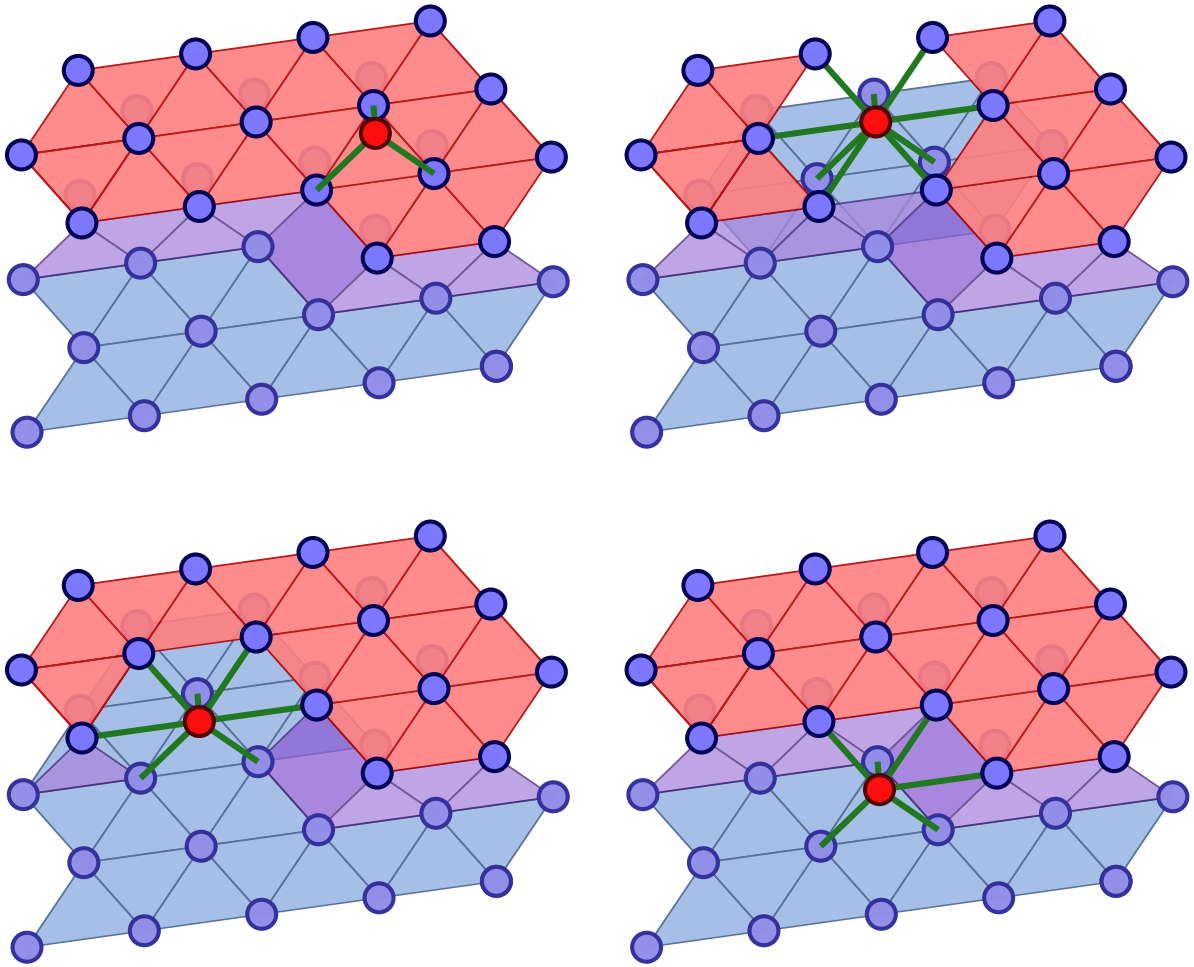
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Energetics of Point Defects

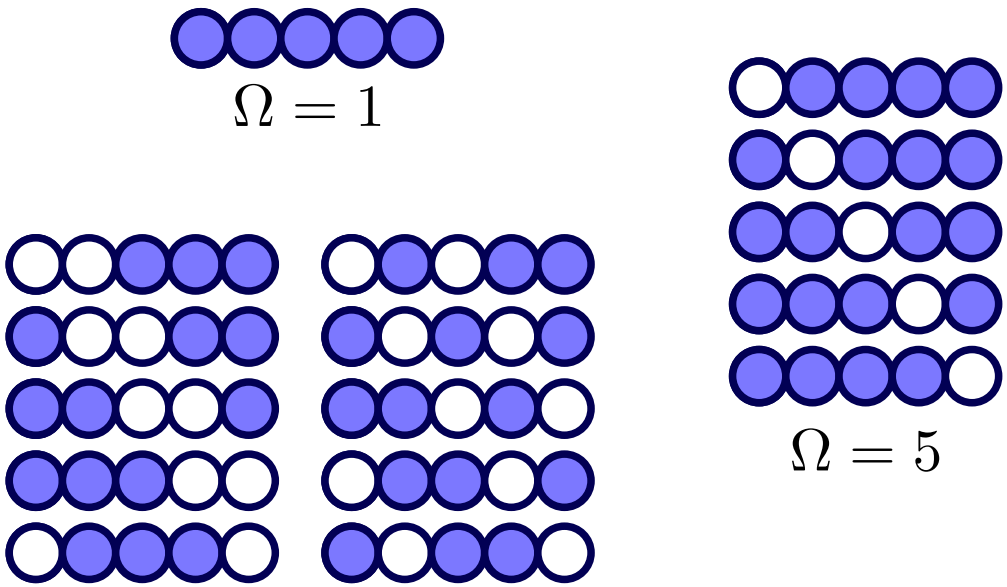
- Let's count the number of intact bonds associated to each surface site on a (111) surface of an *fcc* crystal
- Adatom: 3; Terrace: 9; Ledge: 7; Kink: 6;



Configurational Entropy for a Point Defect

- Entropy is a counter of the number of ways you can realize a thermodynamic state: $S = k_B \ln \Omega$
- n_v vacancies in N states - *Stirling approximation* ($\ln N! \approx N \ln N$)

$$S(n_v) = k_B \ln \frac{N!}{(N - n_v)! n_v!} = k_B \left[N \ln N - (N - n_v) \ln (N - n_v) - n_v \ln n_v \right]$$



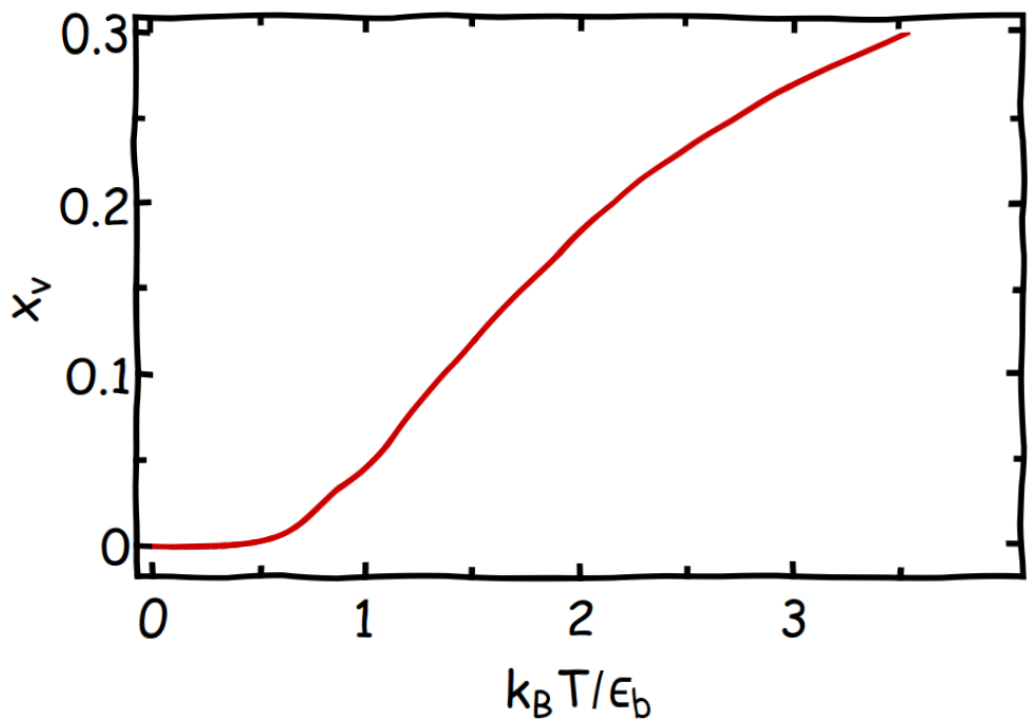
Concentration of Defects in a Solid

- Gibbs free energy for a solid with N sites containing n_v vacancies:

$$G = G_0 + n_v\epsilon_v - k_B T\left[N\ln N - (N-n_v)\ln(N-n_v) - n_v \ln n_v\right]$$

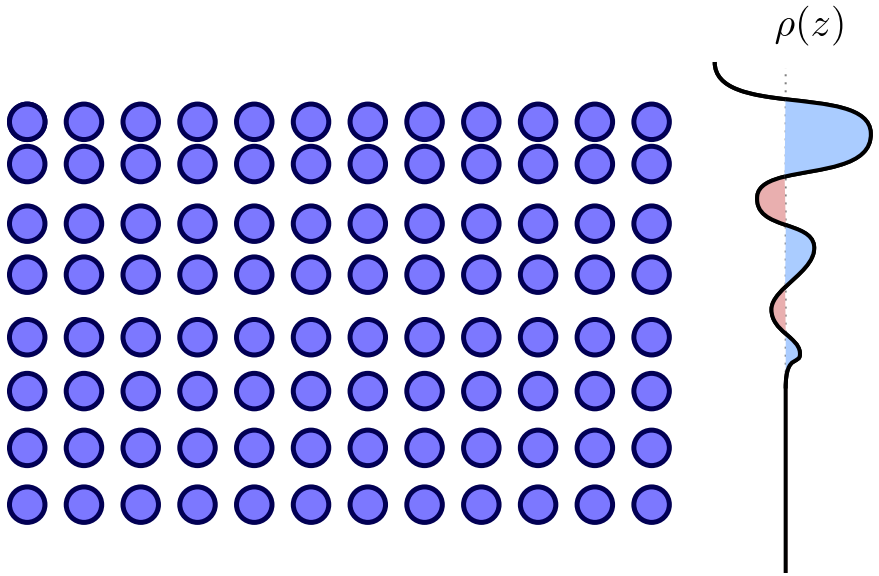
- Energy for creating a vacancy: bulk$\rightarrow$kink $\epsilon_v \approx (12\epsilon_b - 6\epsilon_b) = 6\epsilon_b$
  surf.$\rightarrow$kink $\epsilon_v \approx (9\epsilon_b - 6\epsilon_b) = 3\epsilon_b$
- At equilibrium $\partial G/\partial n_v = 0$

$$\frac{n_v}{N-n_v} = \exp\left(-\frac{\epsilon_v}{k_B T}\right) \longrightarrow \frac{n_v}{N} \approx \frac{1}{1+\exp\left(\frac{\epsilon_v}{k_B T}\right)}$$



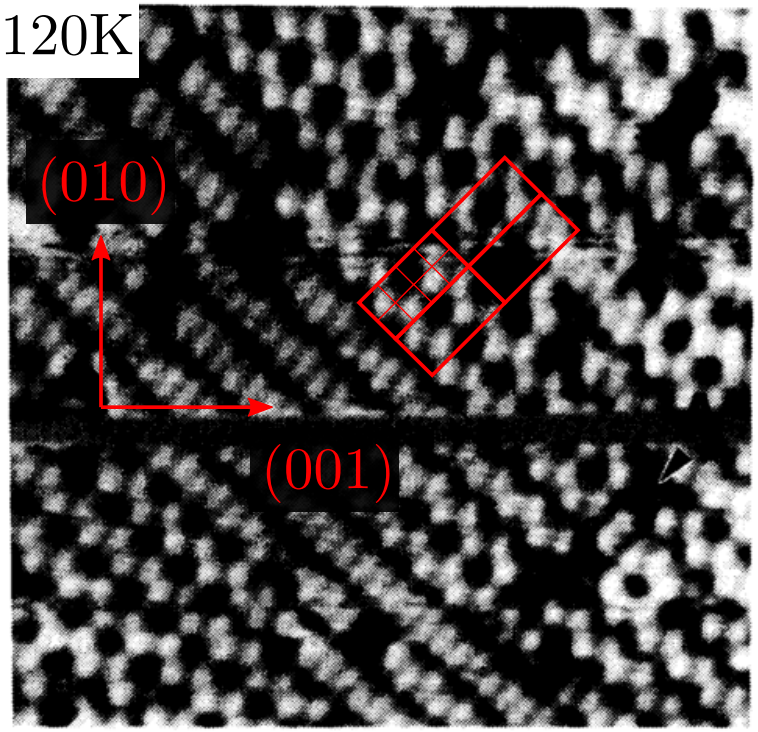
Surface relaxation

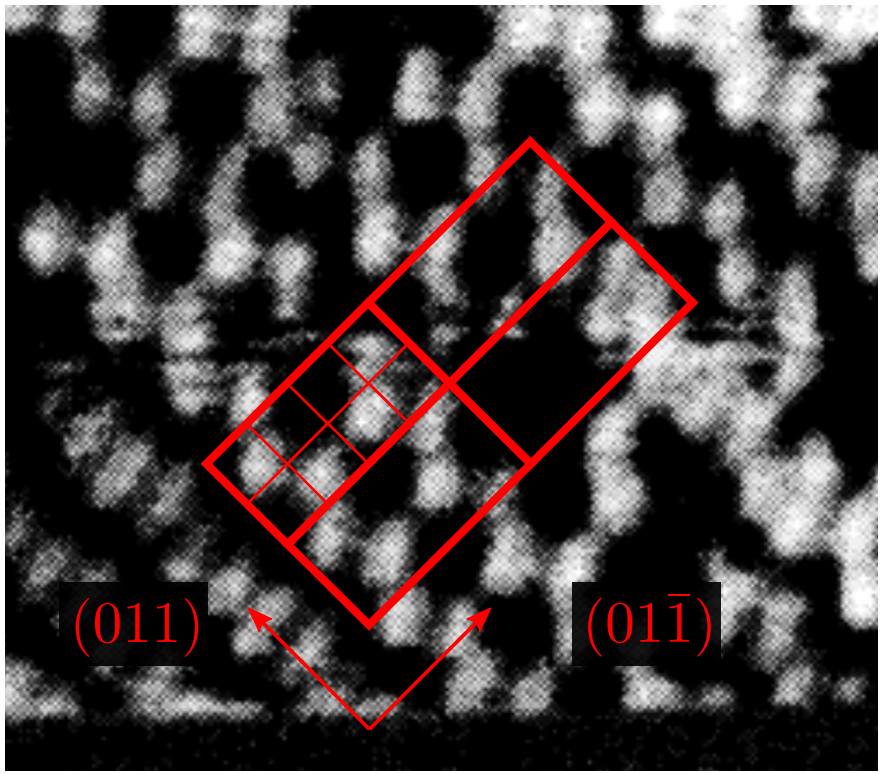
- Atoms at a freshly-cut surface do not stay fixed at bulk-like positions, but they relax to minimize their energy
- Charge-density effects can lead to oscillations of lattice parameters extending several layers below the surface



Surface Reconstructions

- Real surfaces can display different symmetry than a “truncated bulk” [e.g. Si(100)]
- **Reconstructions** lowers surface energy by forming new bonds

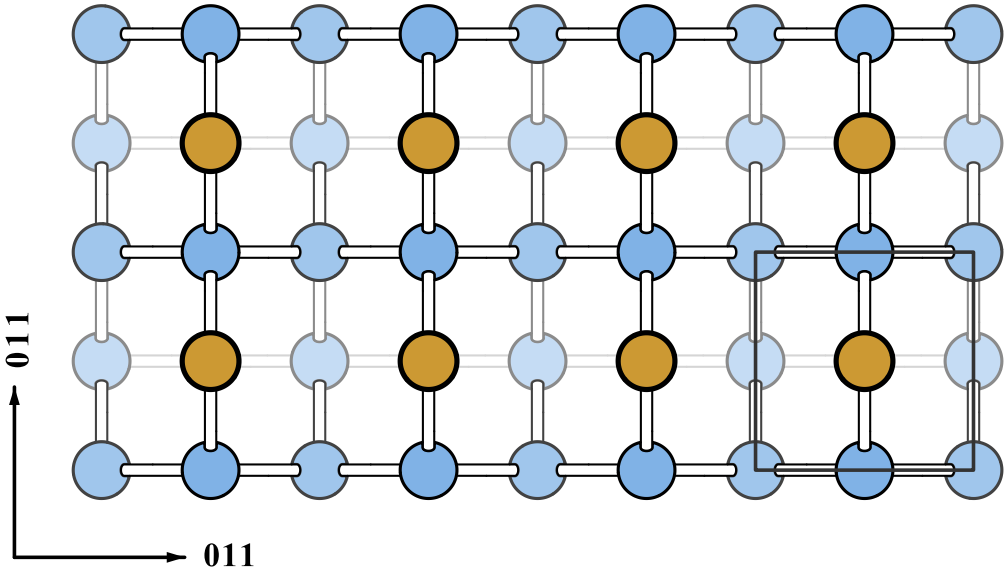


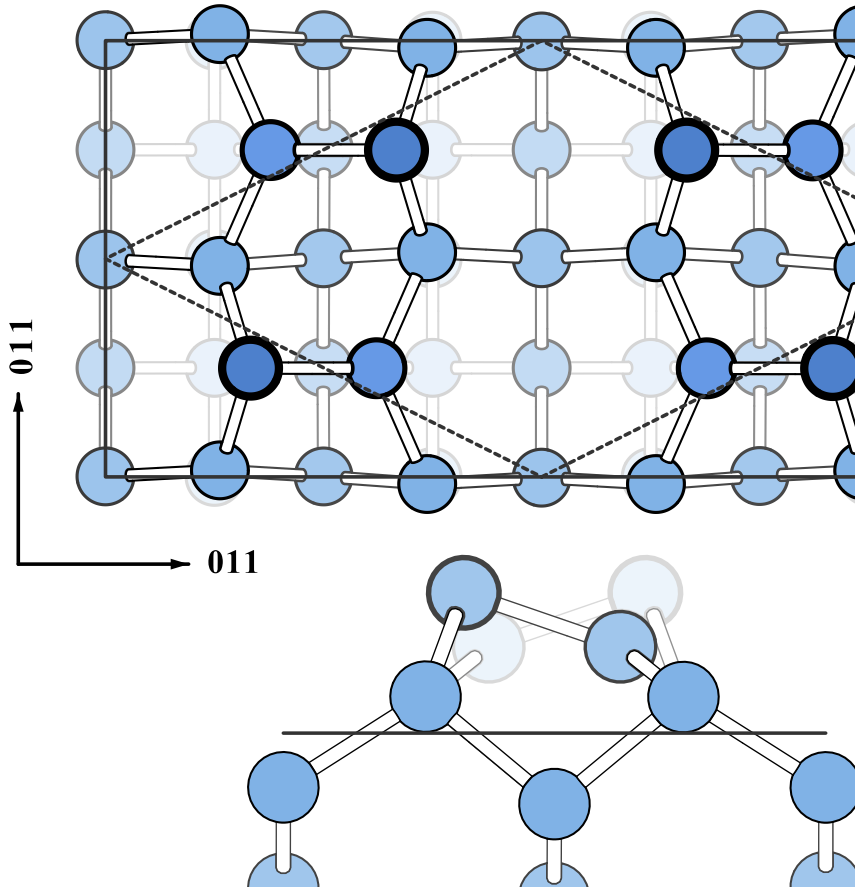


R. Wolkow, PRL 1992

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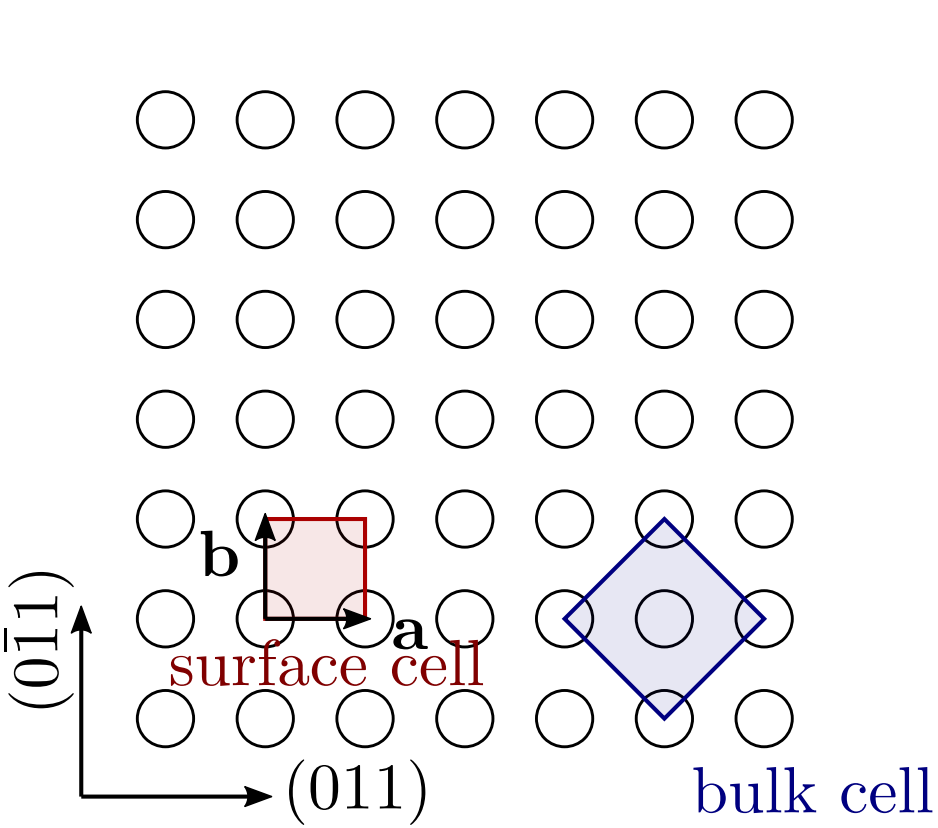


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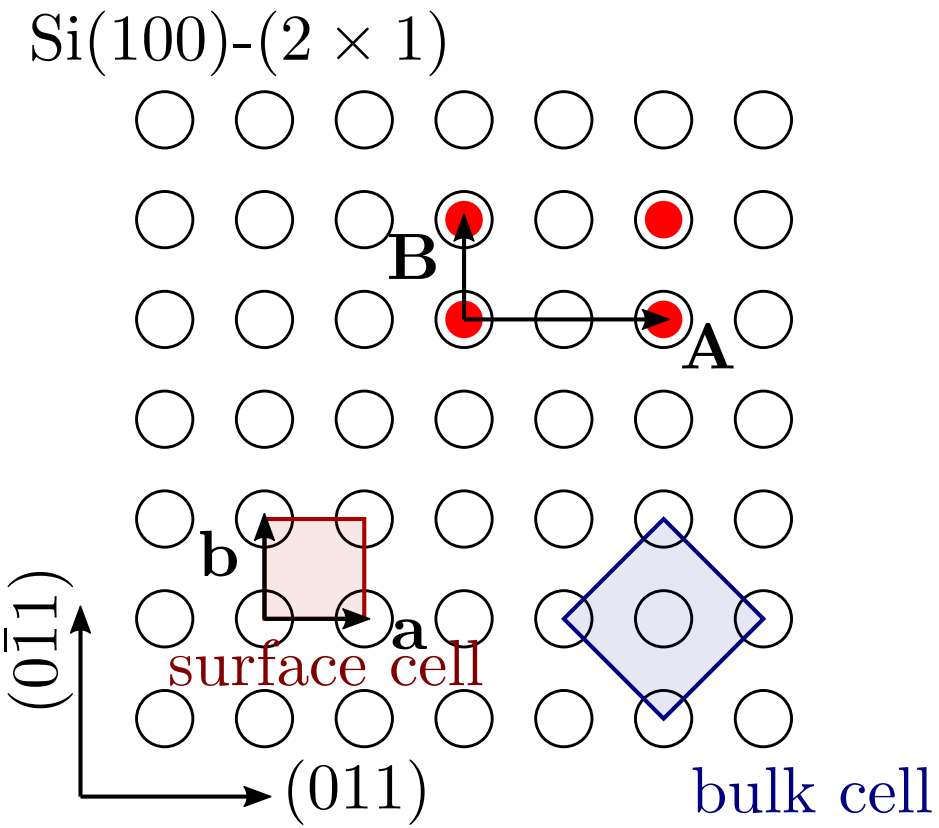
Nomenclature For Surface Crystallography

- The unit cell of a (reconstructed) surface is often labeled relative to the clear-cut lattice vectors (Wood notation)

$$M\,(hkl) - [c|p]\,(m \times n)\,[R\alpha]$$



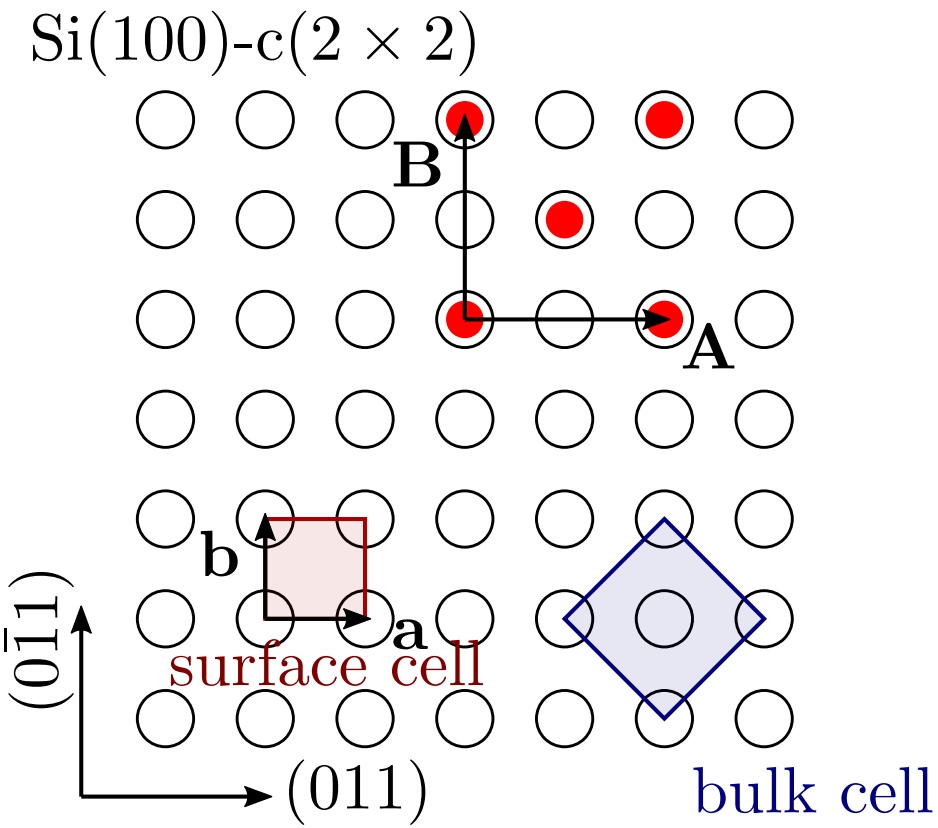
$\mathrm{Si}(100)\text{-}(2 \times 1)$

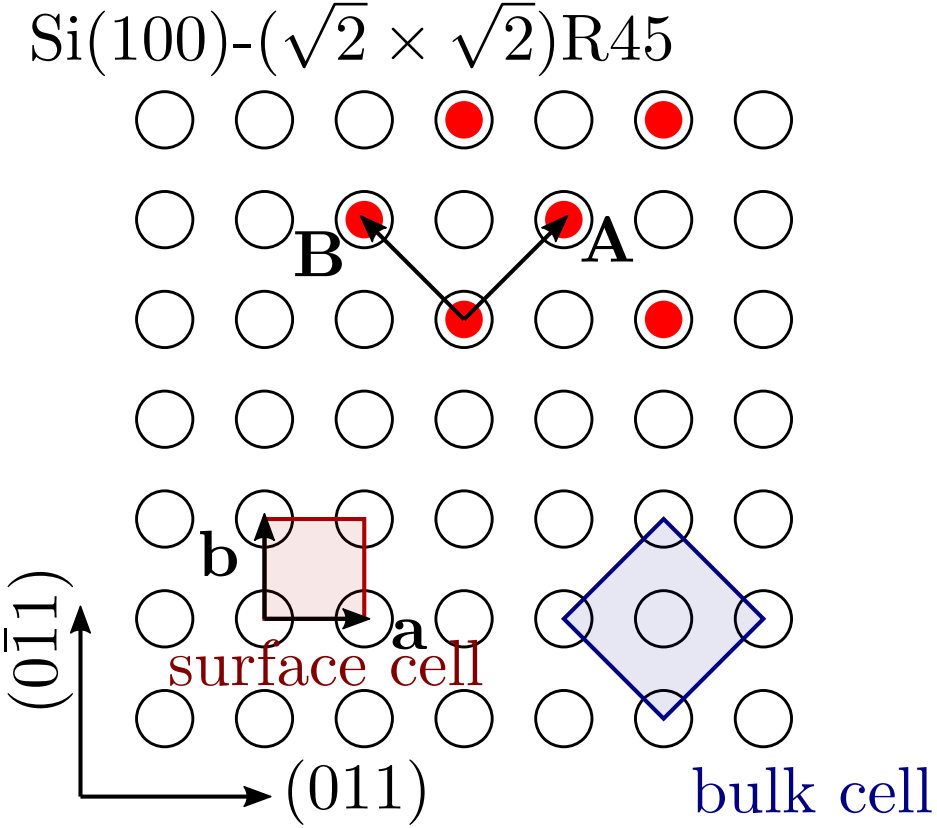


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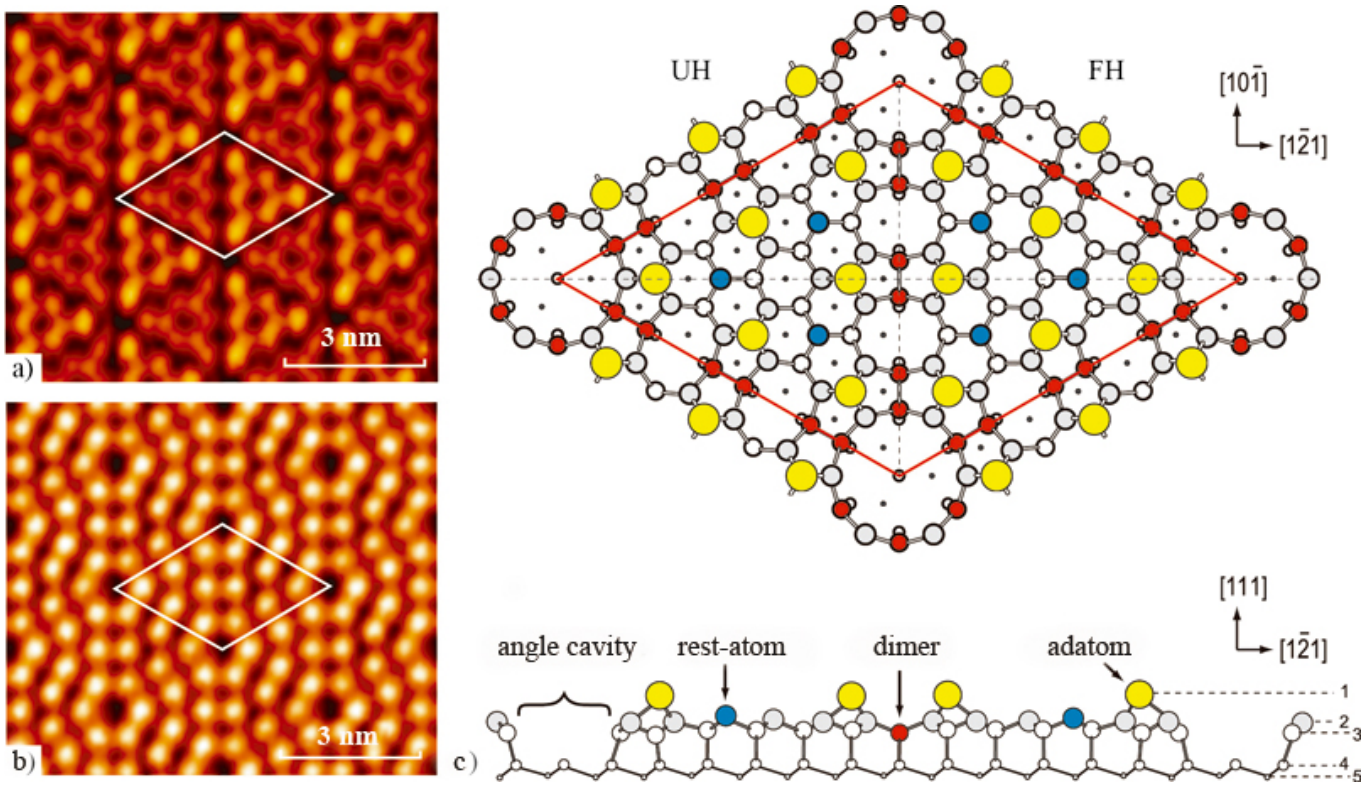




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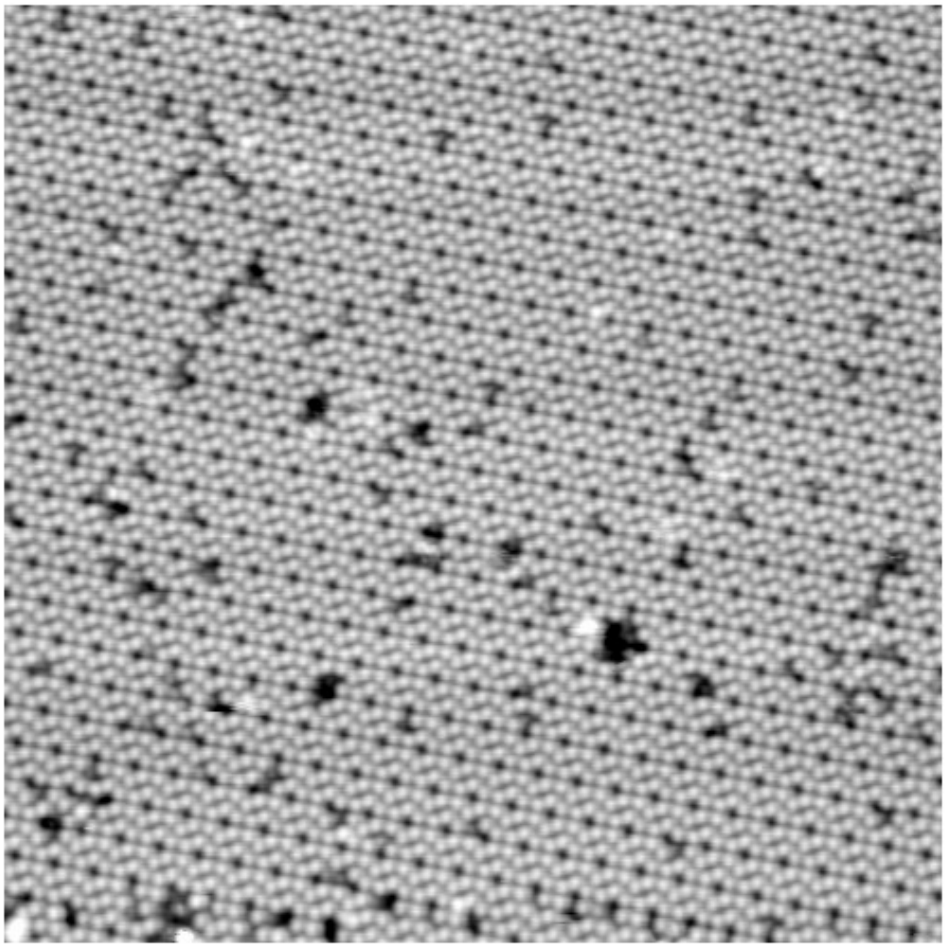
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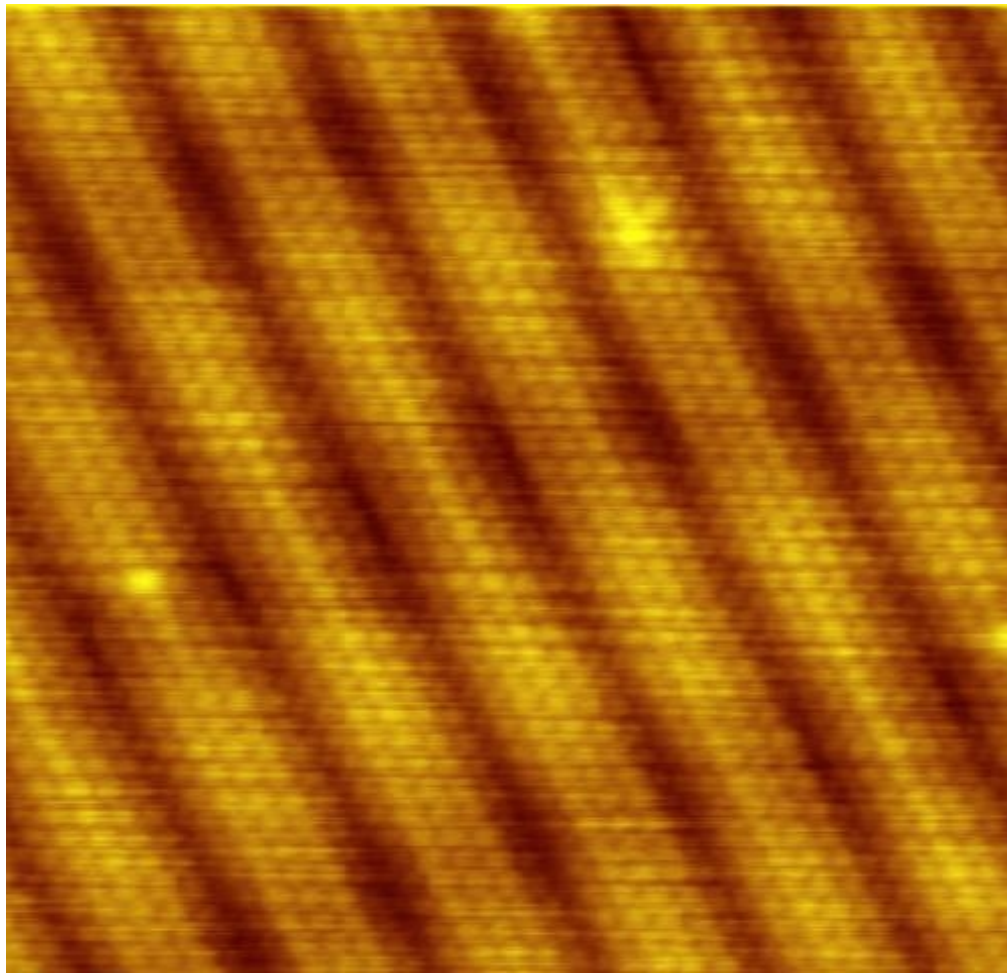
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Si(111)-(5 × 5)



Au(100)-(28 × 5)