

Površina

IDEJA: Kada se formira površina raspored atoma na površini ostaje sličan kao u kristalu

SADRŽAJ 1.2.

Čvrsta površina

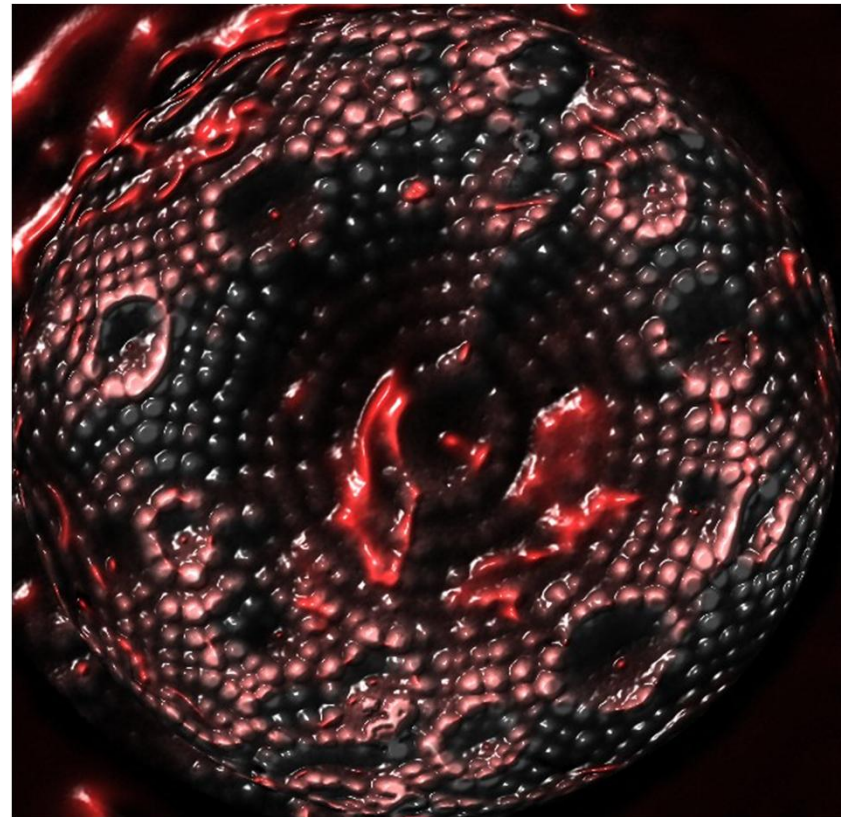
Kristalna struktura

Elektronska struktura

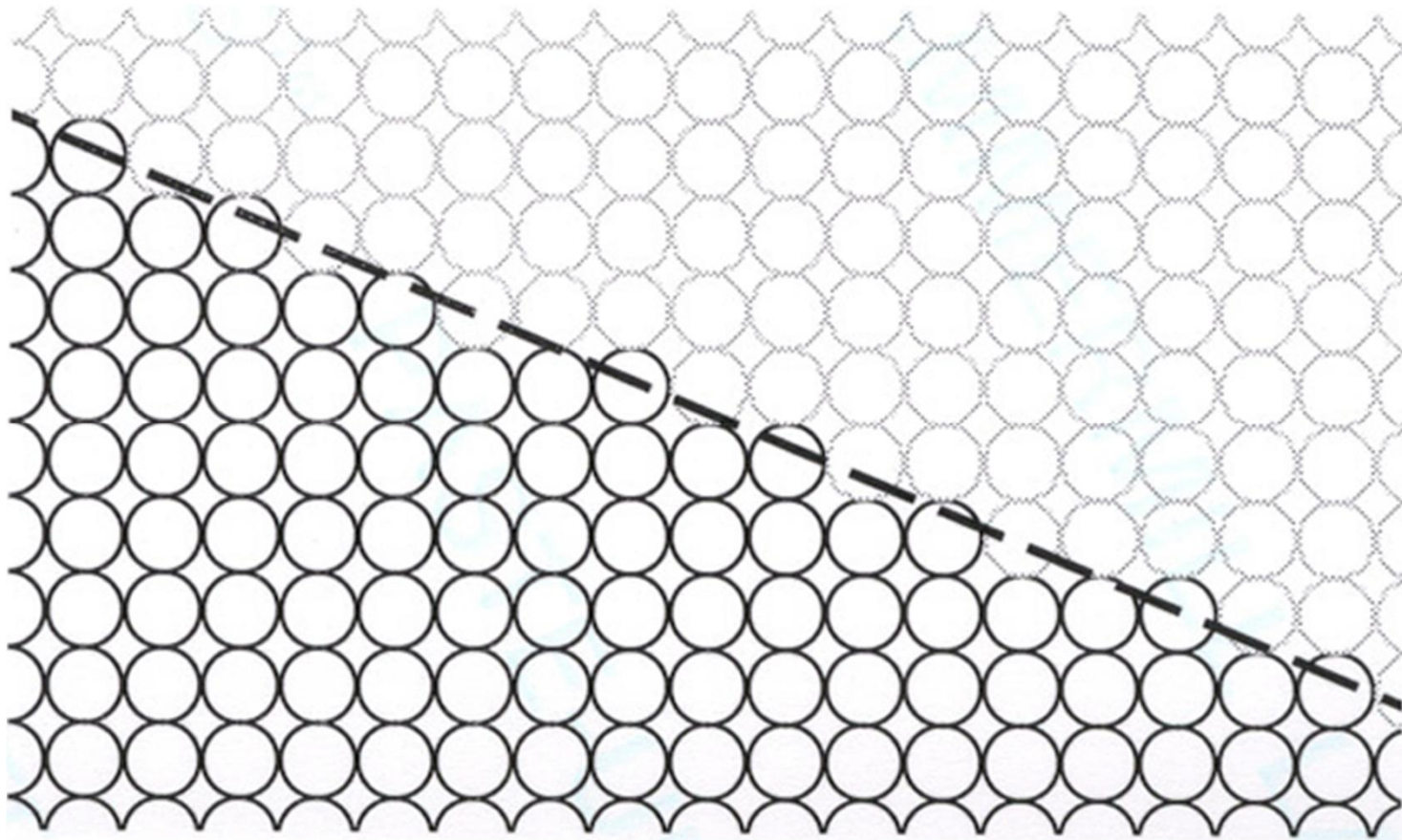
Rekonstrukcija i relaksacija

Volframova igla

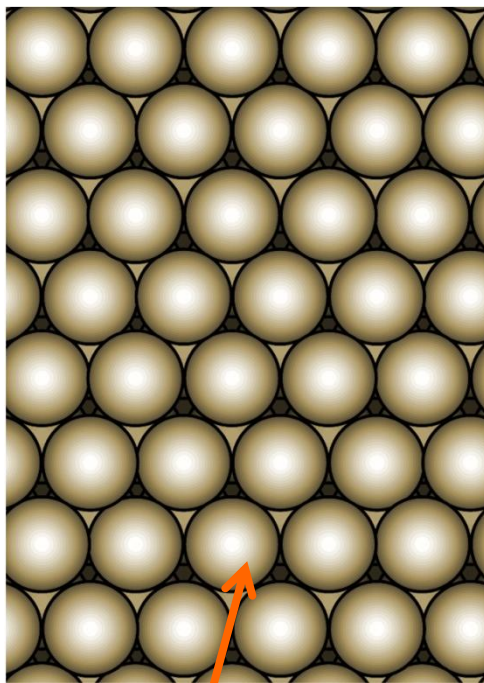
J. Chem. Phys. 124, 204716 (2006)



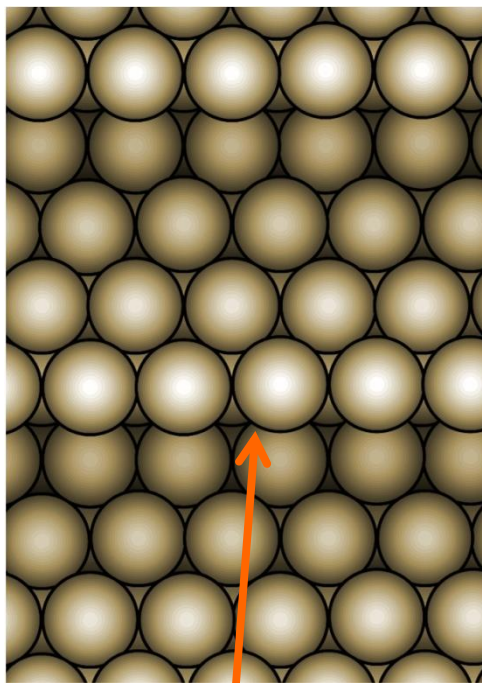
Formiranje površine



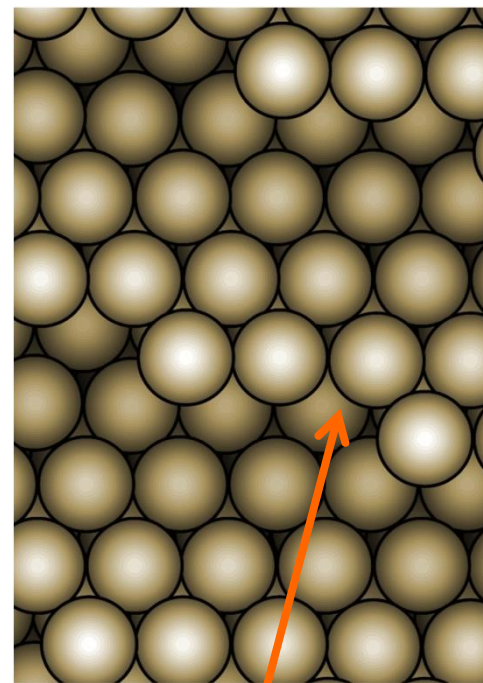
Neke od karakterističnih lokalnih struktura na površinama



Terasa



Stepenik



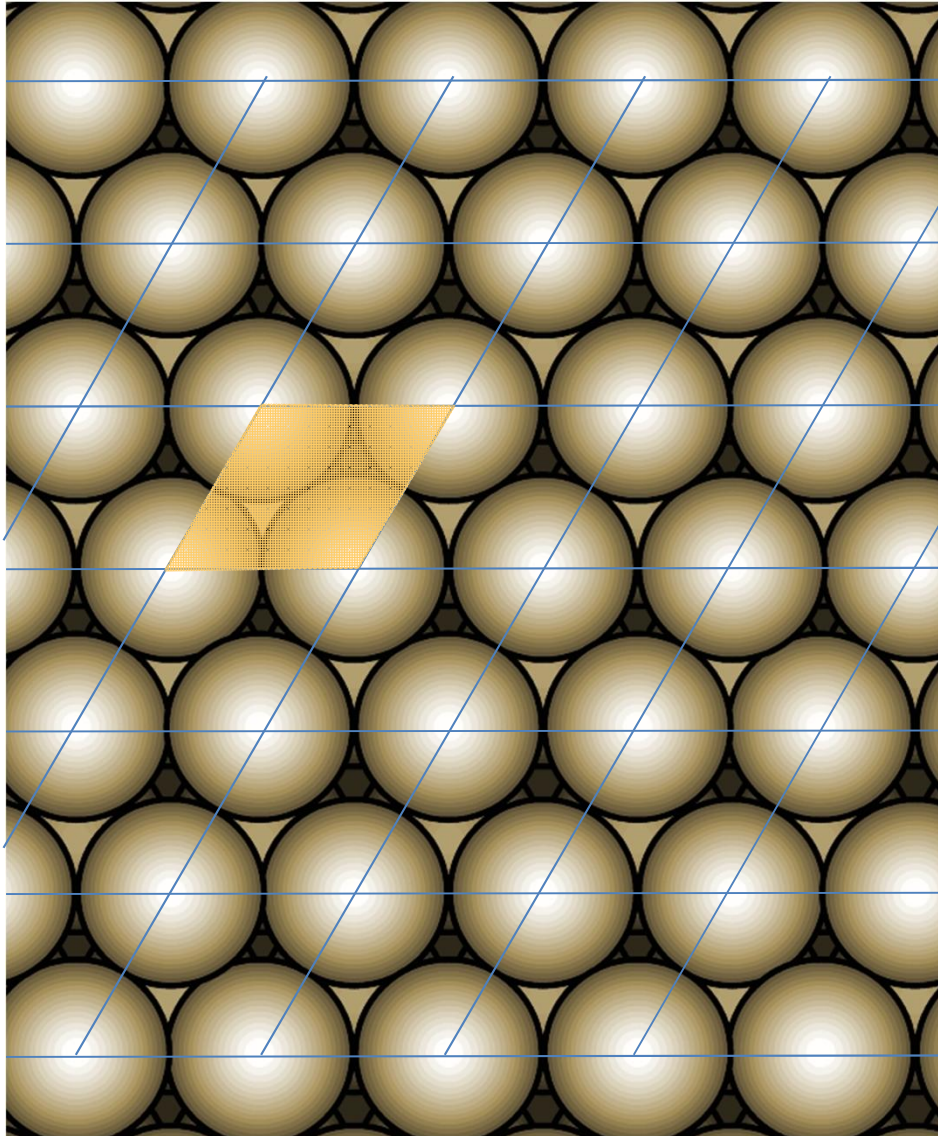
Kink

Notacija površinskih struktura

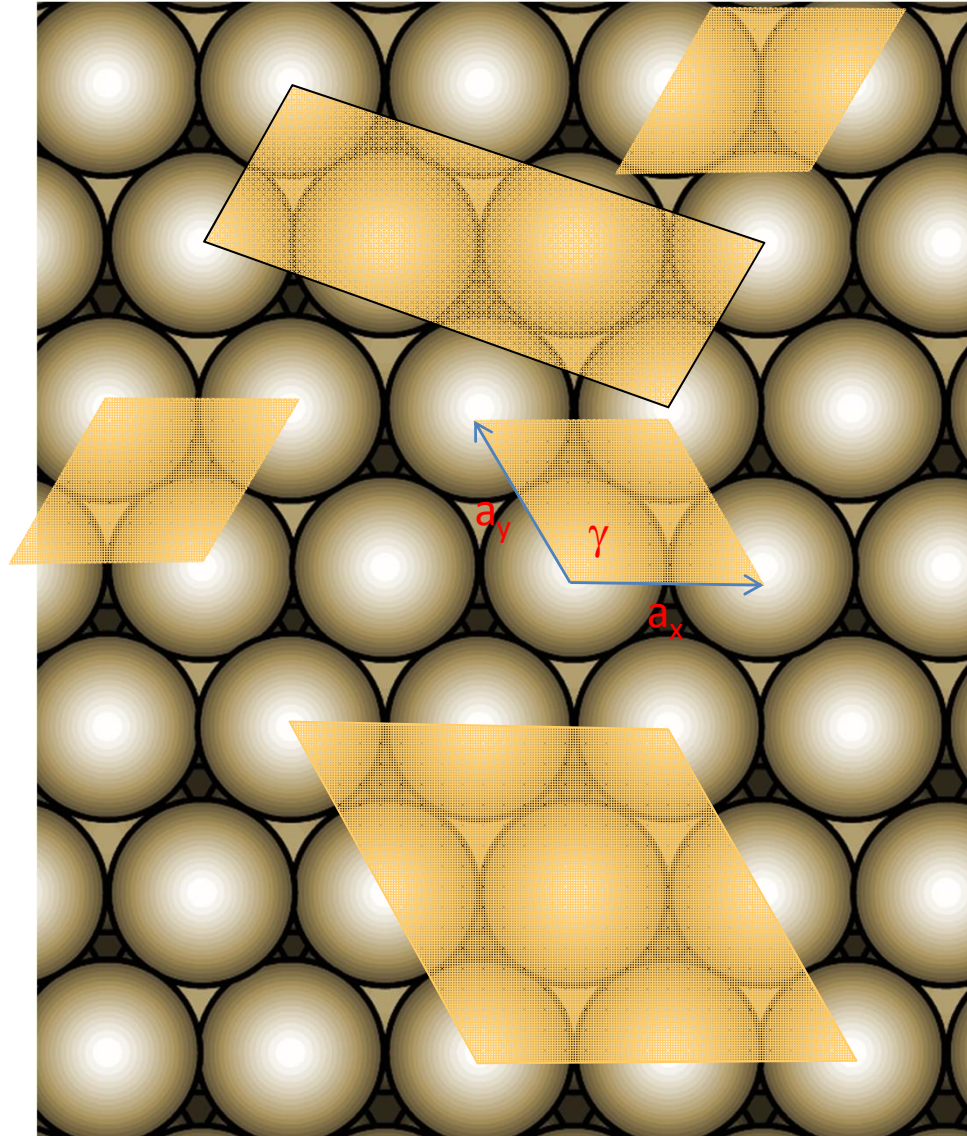
Ideja:

- Osnovna ponavljajuća jedinica na površini – jedinična ćelija
- Razviti notaciju za opis jedinične ćelije

Jedinična površinska ćelija



Izbor nije jedinstven



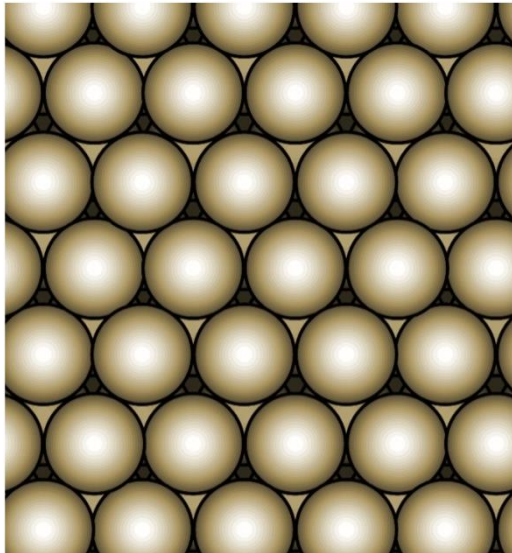
2D Bravaisove rešetke

Ideja – klasifikovati jediničnu ćeliju prema simetriji

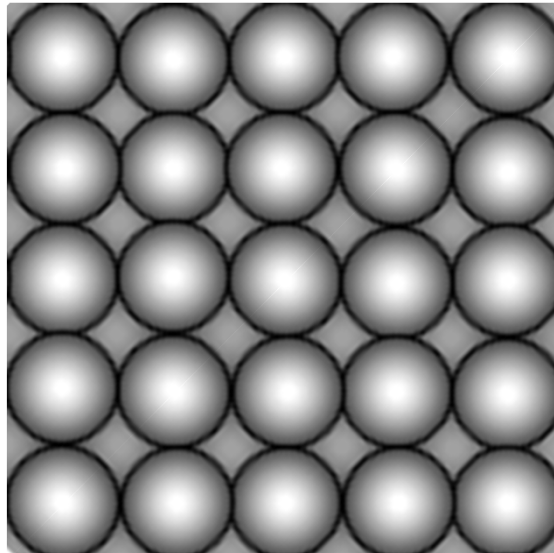
6 Bravaisovih rešetki u 2D

		Conventional	Axes of Conventional
Lattice	Axes of Primitive Cell	Cell	Cell
Oblique	$a_x \neq a_y, \gamma \neq 90^\circ \text{ or } 120^\circ$	Parallelogram	$a_x \neq a_y, \gamma \neq 90^\circ \text{ or } 120^\circ$
Centered rectangle	$a_x = a_y, \gamma \neq 90^\circ \text{ or } 120^\circ$	Rectangle	$a_x' \neq a_y', \gamma' = 90^\circ$
Primitive rectangle	$a_x \neq a_y, \gamma = 90^\circ$	Rectangle	$a_x \neq a_y, \gamma = 90^\circ$
Hexagonal	$a_x = a_y, \gamma = 120^\circ$ with a sixfold axis	Hexagonal	$a_x = a_y, \gamma = 120^\circ$
Oblique	$a_x \neq a_y, \gamma = 120^\circ$	Parallelogram	$a_x \neq a_y, \gamma = 120^\circ$
Square	$a_x = a_y$	90° square	$a_x = a_y, \gamma = 90^\circ$

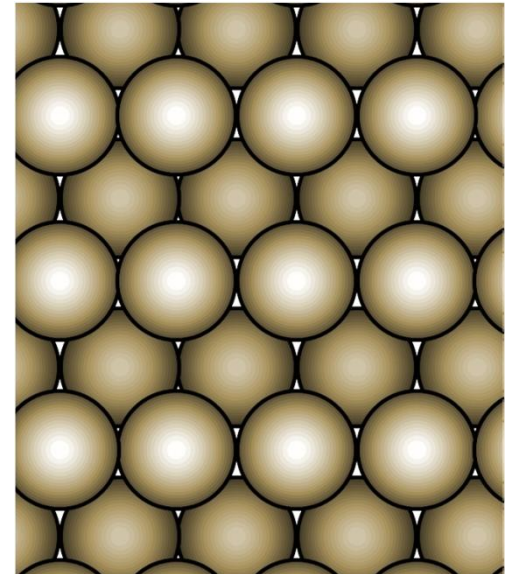
Šestougao



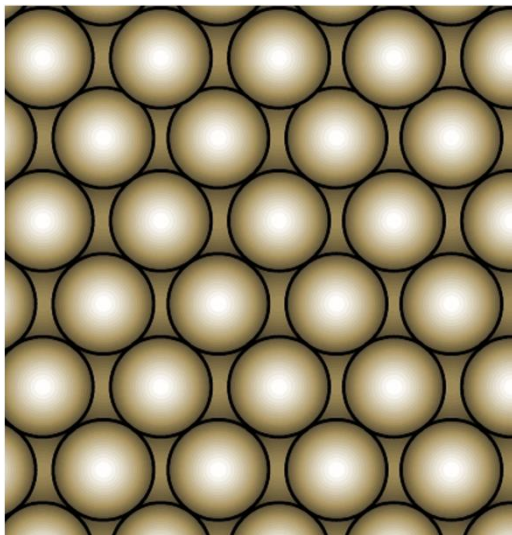
Kvadrat



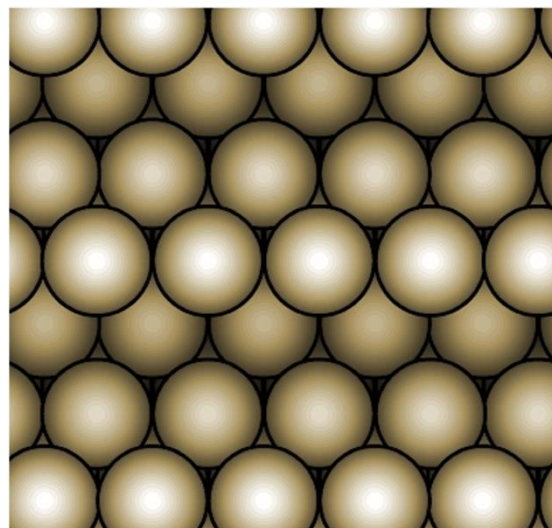
Pravougaonik



Centrirani pravougaonik

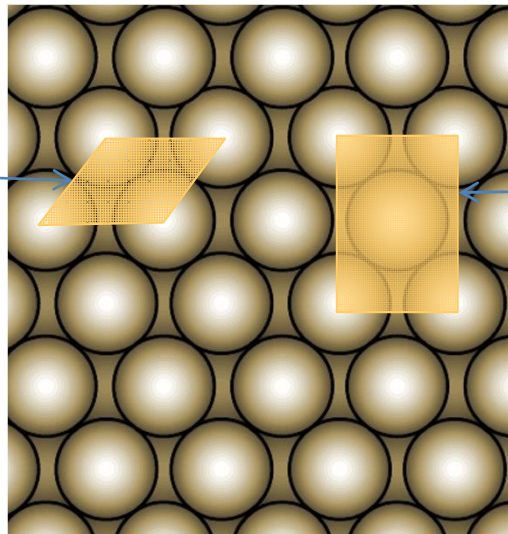


Pravougaonik



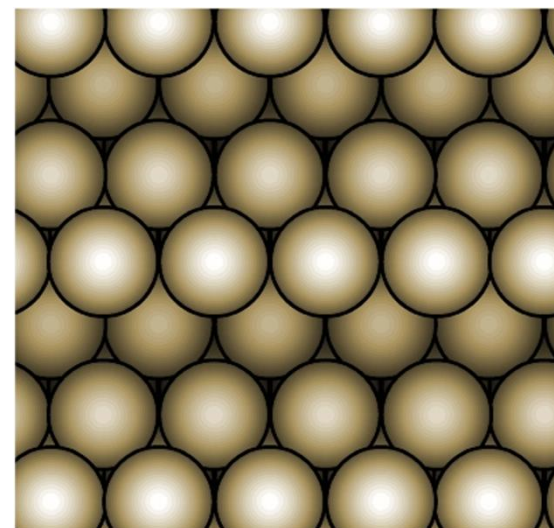
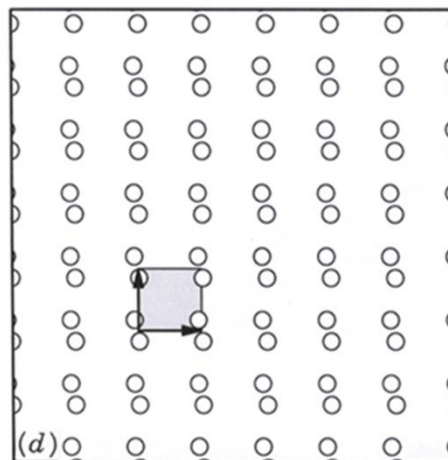
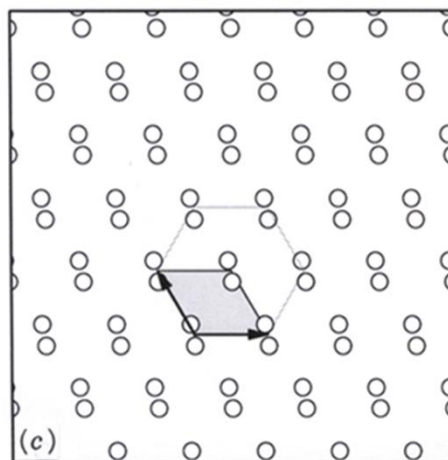
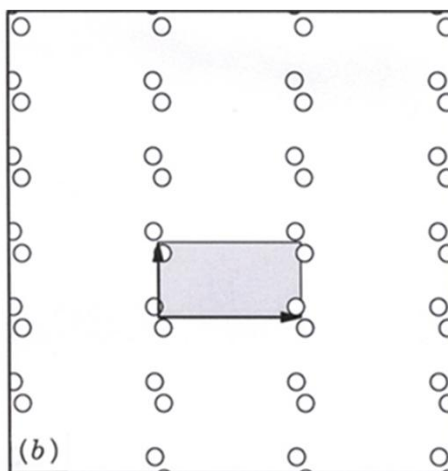
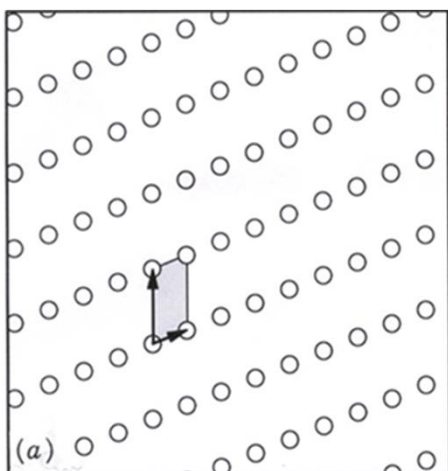
Centrirani pravougaonik

Primitivna
ćelija



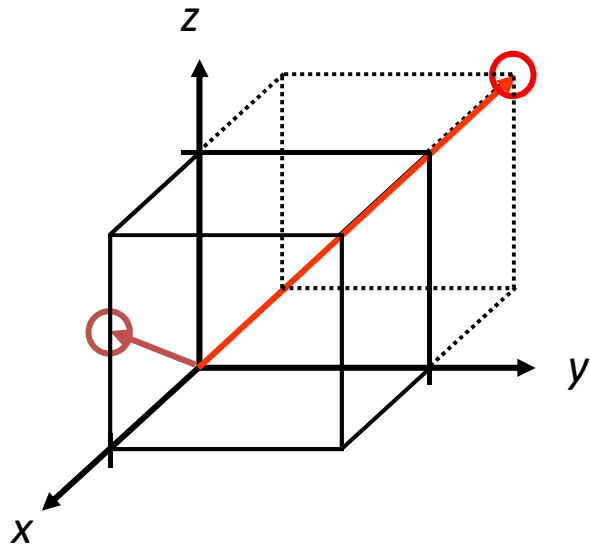
Konvencionalna
jedinična ćelija

Jedinična ćelija + strukturni motiv



Kristalografski pravci

Algoritam



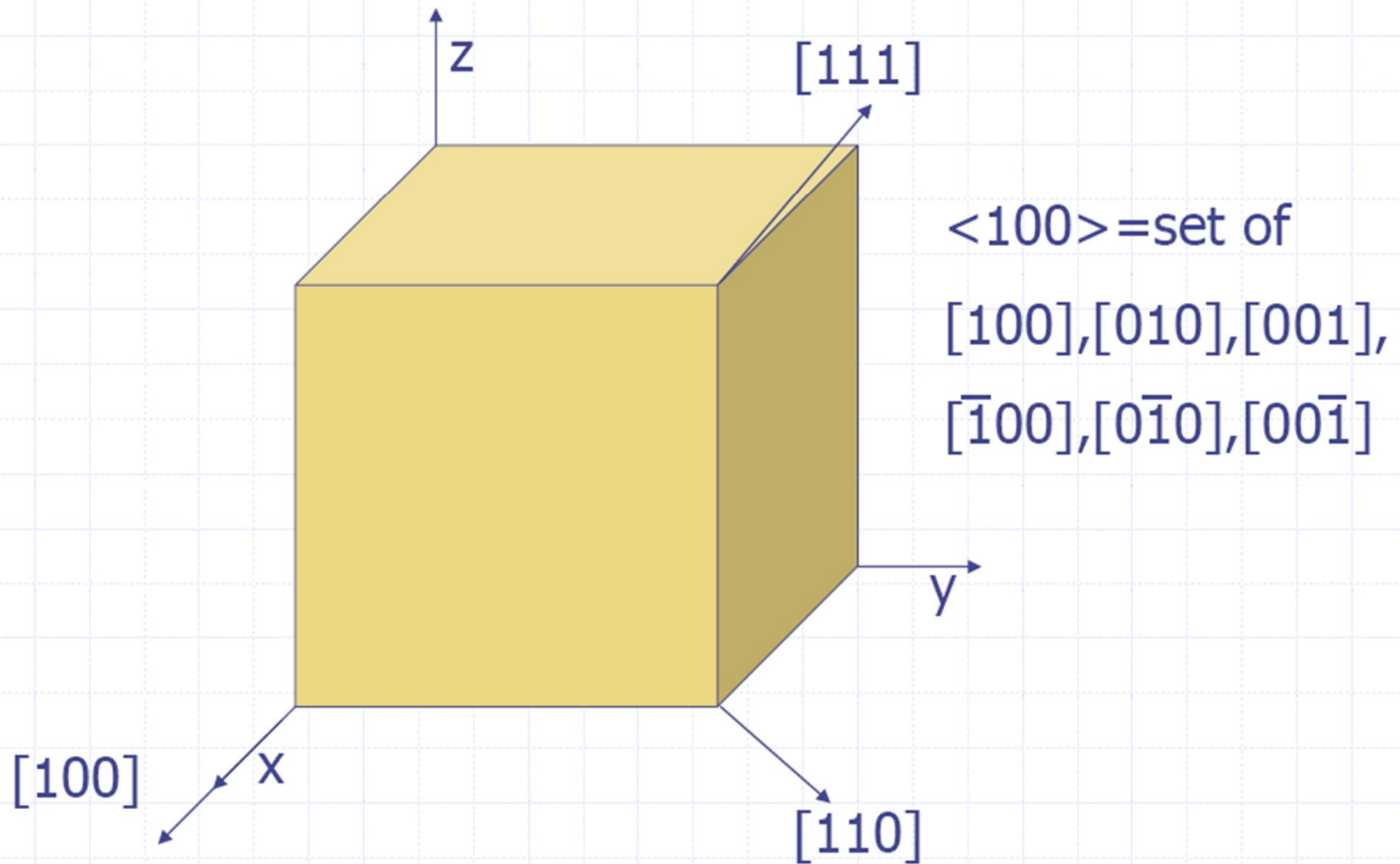
1. Pomeriti vektor da prolazi kroz (0,0,0)
2. Pročitati projekcije u umnošku a, b i c
3. Podesiti na najmanje cele brojeve
4. dati u fomi $[uvw]$

primer: $1, 0, \frac{1}{2}$ $\Rightarrow 2, 0, 1$ $\Rightarrow [201]$

$-1, 1, 1$ $\Rightarrow [\bar{1}11]$ Negativan indeks – crtica iznad

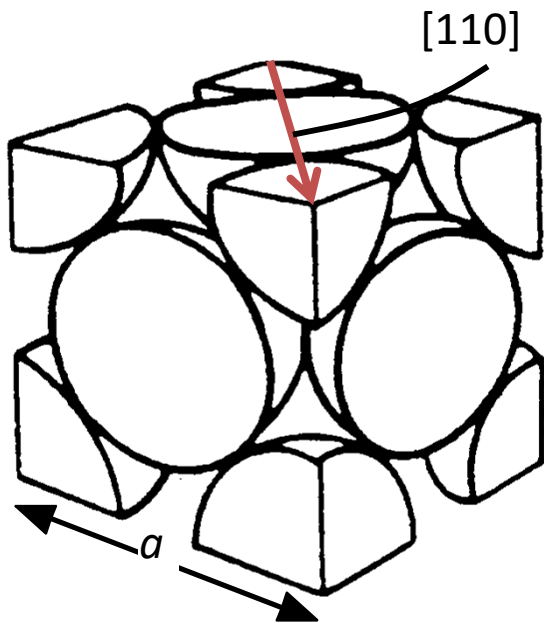
Familija pravaca $\langle uvw \rangle$

Miller indices: Directions



Linearna gustina

- Linearna gustina atoma $\equiv$ LD = $\frac{\text{Broj atoma}}{\text{Jedinica dužine vektora}}$

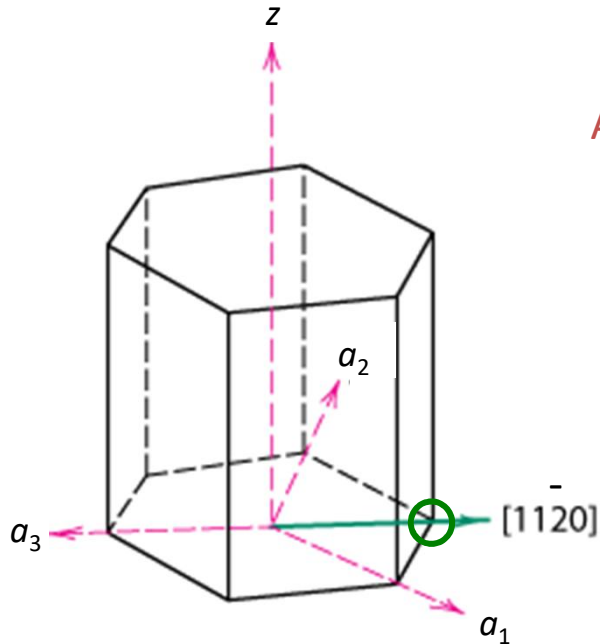


primer: linearna gustina Al u pravcu $[110]$

$$a = 0.405 \text{ nm}$$

$$\text{LD} = \frac{\overset{\text{\# atoma}}{2}}{\underset{\text{dužina}}{\sqrt{2}a}} = 3.5 \text{ nm}^{-1}$$

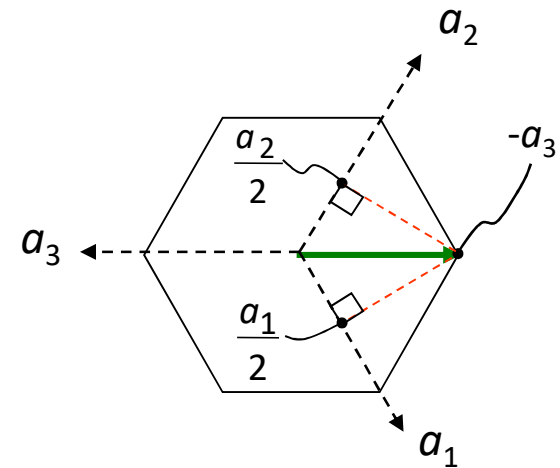
HCP kristalograski pravci



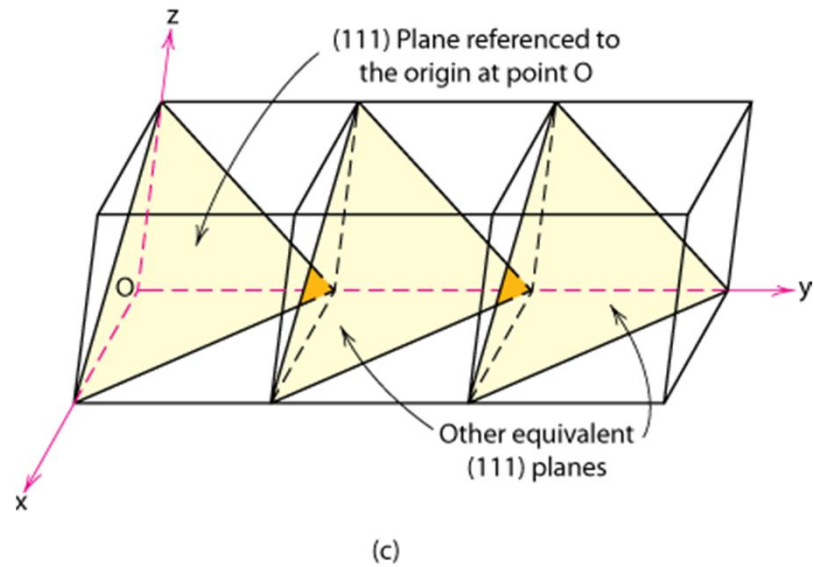
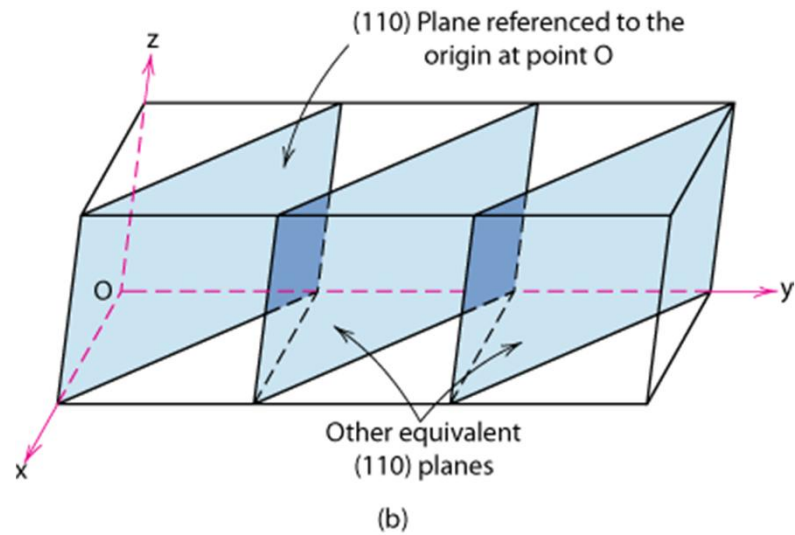
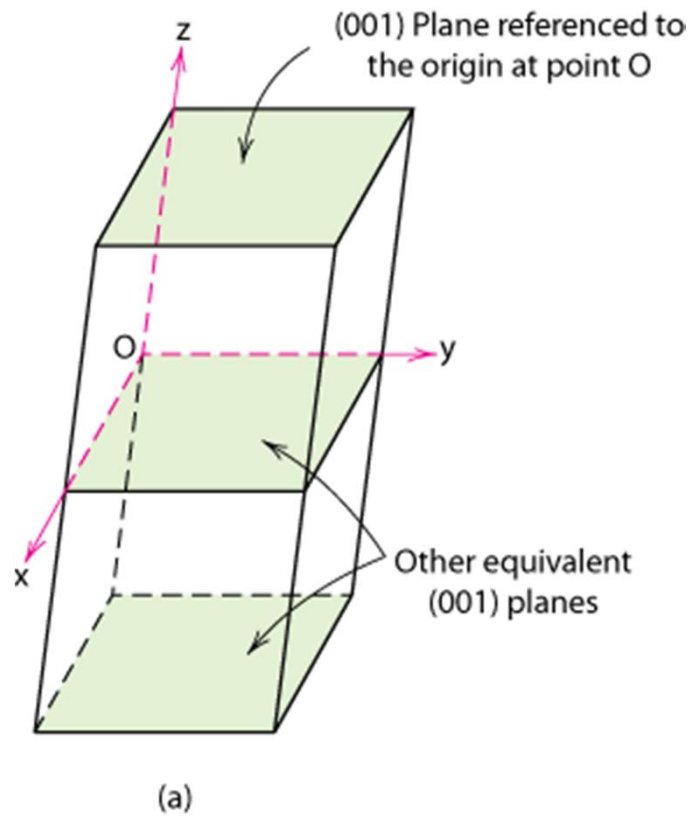
Algoritam

1. Pomeriti vektor da prolazi kroz $(0,0,0)$
2. Pročitati projekcije u umnošku a , b i c
3. Podesiti na najmanje cele brojeve
4. dati u fomi $[uvw]$

Primer: $\frac{1}{2}, \frac{1}{2}, -1, 0 \Rightarrow [11\bar{2}0]$



Kristalografske ravni



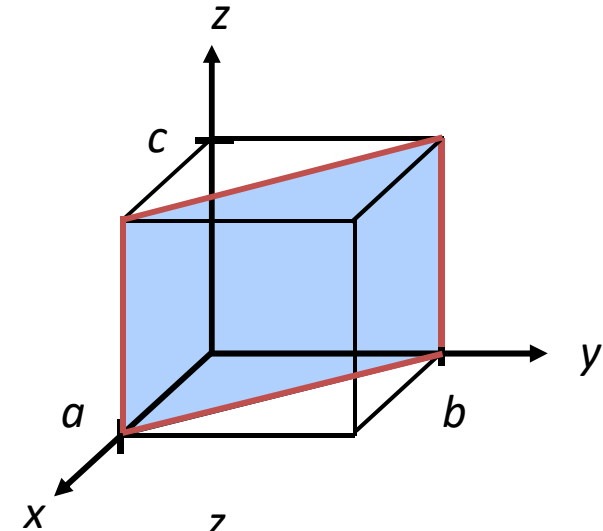
Kristalografske ravni

- Milerovi indeksi: kako se određuju?
- Sve paralelne ravni imaju iste Milerove indekse.
- Algoritam
 1. Očitati preseke ravni sa a , b , c
 2. Uzeti recipročne vrednosti odsečaka
 3. Redukovati na najmanje cele brojeve
 4. U zagrade, bez zareza (hkl)

Kristalografske ravni

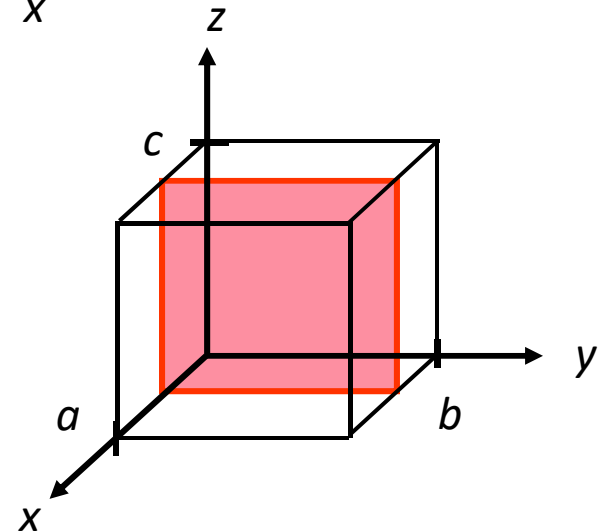
Primer

	a	b	c
1. Preseci	1	1	∞
2. Recipročno	$1/1$	$1/1$	$1/\infty$
	1	1	0
3. Redukcija	1	1	0
4. Milerovi indeksi	(110)		



Primer

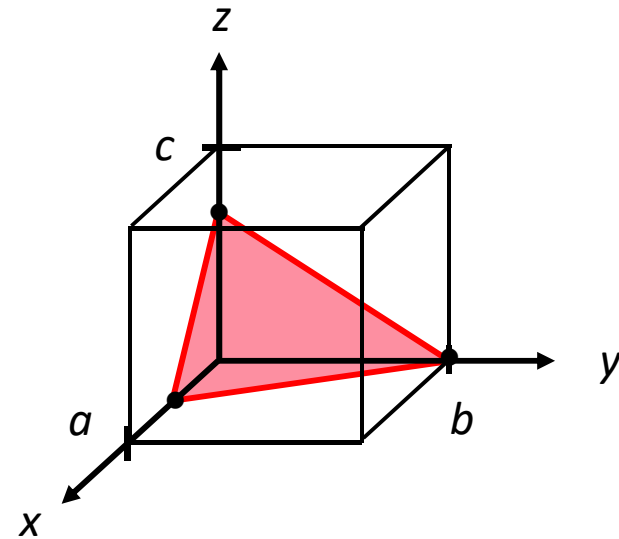
	a	b	c
1. Preseci	$1/2$	∞	∞
2. Recipročno	$1/1/2$	$1/\infty$	$1/\infty$
	2	0	0
3. Redukcija	2	0	0
4. Milerovi indeksi	(200)		



Kristalografske ravni

Primer

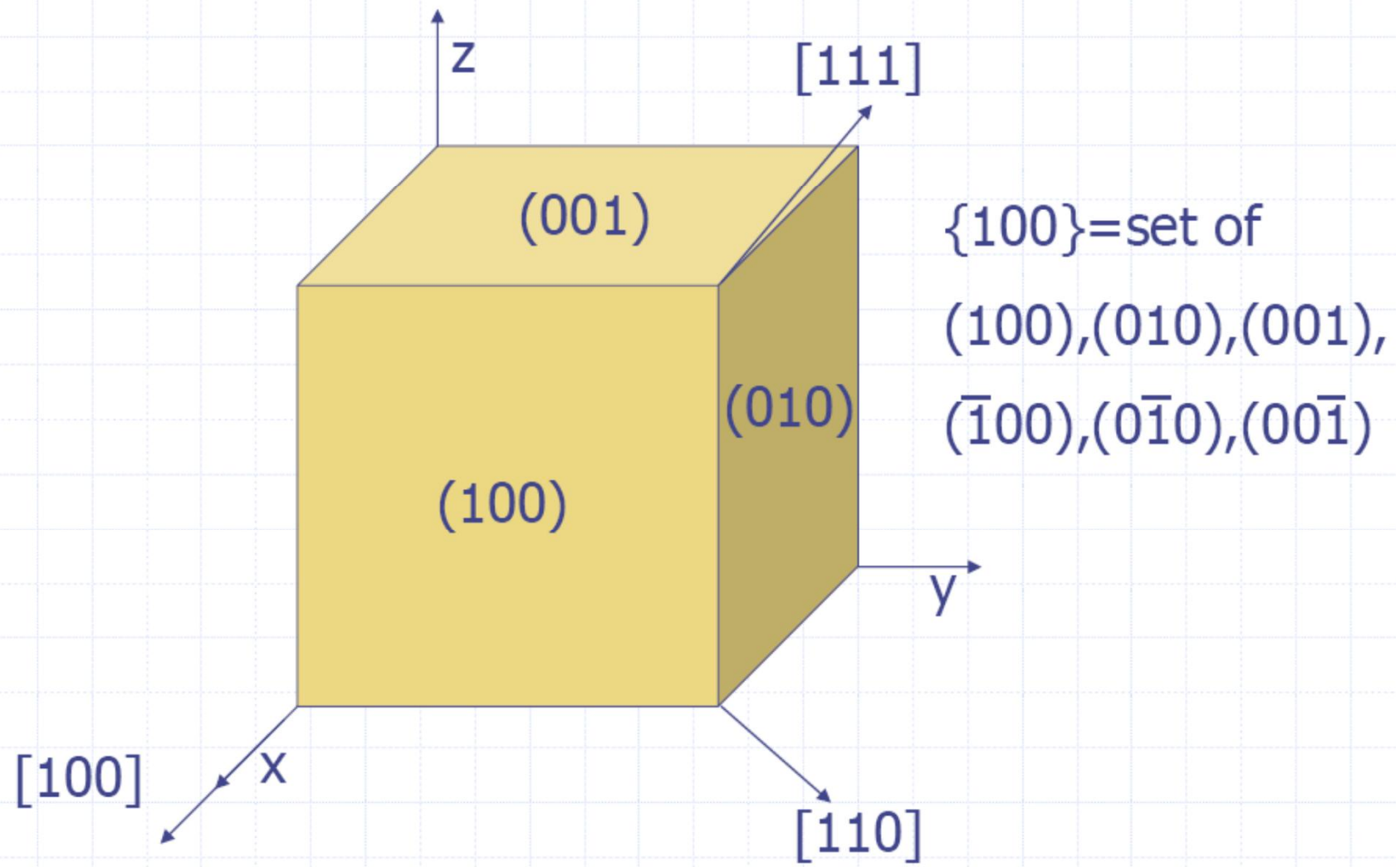
	a	b	c
1. Preseci	$1/2$	1	$3/4$
2. Recipročno	$1/1/2$	$1/1$	$1/3/4$
	2	1	$4/3$
3. Redukcija	6	3	4
4. Millerovi indeksi	(634)		



Porodica ravni $\{hkl\}$

Primer: $\{100\} = (100), (010), (001), (\bar{1}00), (0\bar{1}0), (00\bar{1})$

Miller indices: Planes

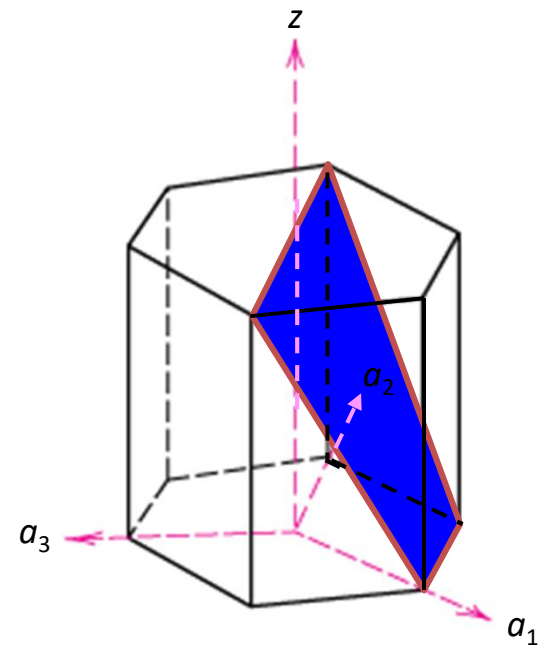


Heksagonalni sistem (HCP)

- Ista ideja

Primer

	a_1	a_2	a_3	c
1. Preseci	1	∞	-1	1
2. Recipročno	1	$1/\infty$	-1	1
	1	0	-1	1
3. Redukcija	1	0	-1	1
4. Indeksi	$(10\bar{1}1)$			

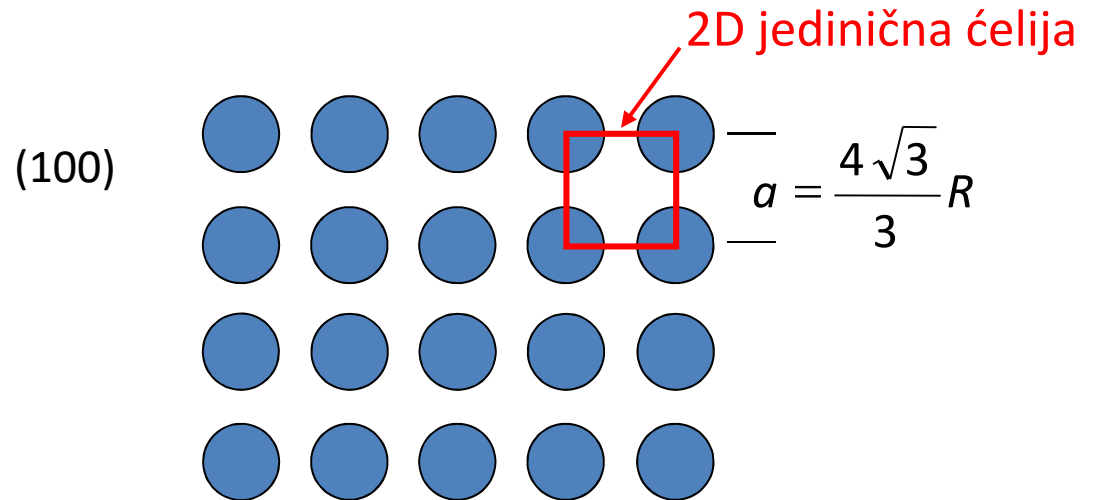
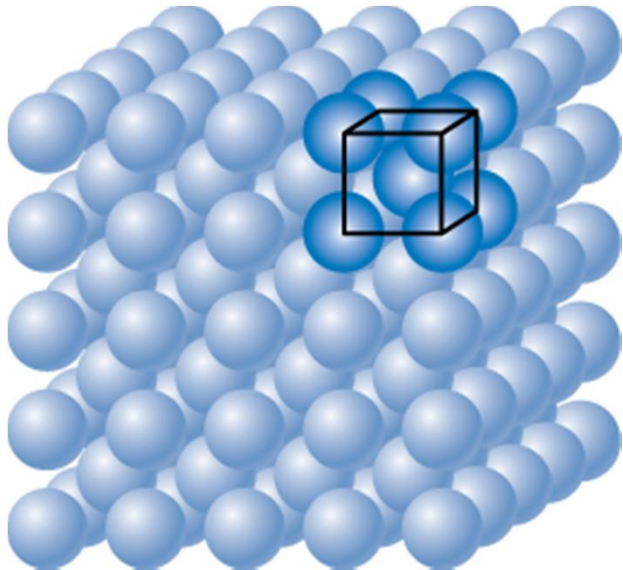


Površinska gustina

- Utiče na površinsku energiju
- Stabilnost površine
- Reaktivnost površine

Površinska gustina Fe(100)

$T < 912^\circ\text{C}$ BCC struktura.

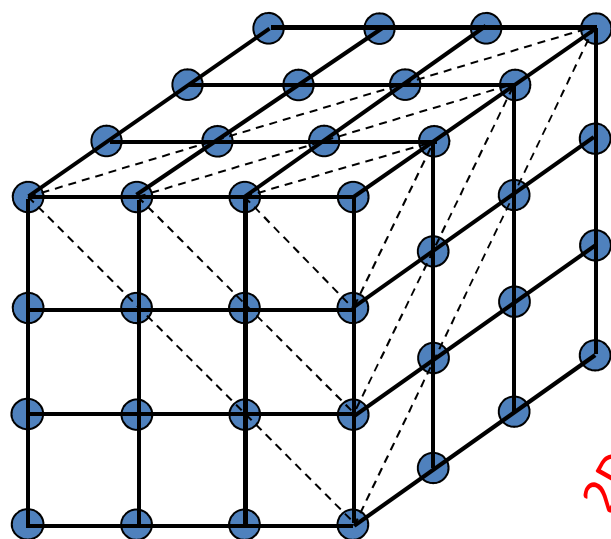


Radijus atoma $R = 0.1241 \text{ nm}$

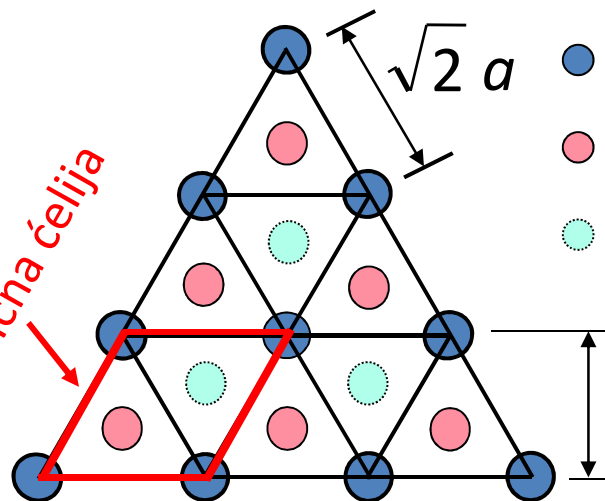
$$\text{Površinska gust} = \frac{\text{atoma}}{\text{2D jed. ćeliji}} = \frac{1}{\text{površina}} = \frac{1}{\text{2D jed ćelija}} = \frac{1}{\left(\frac{4\sqrt{3}}{3}R\right)^2} = 12.1 \frac{\text{atoma}}{\text{nm}^2} = 1.2 \times 10^{19} \frac{\text{atoma}}{\text{m}^2}$$

Površinska gustina Fe(111)

1 atom u ravni/ jedinična ćelija



2D jedinična ćelija



● atomi u ravni

● Atomi iznad ravni

● Atomi ispod ravni

$$h = \sqrt{\frac{3}{2}}a$$

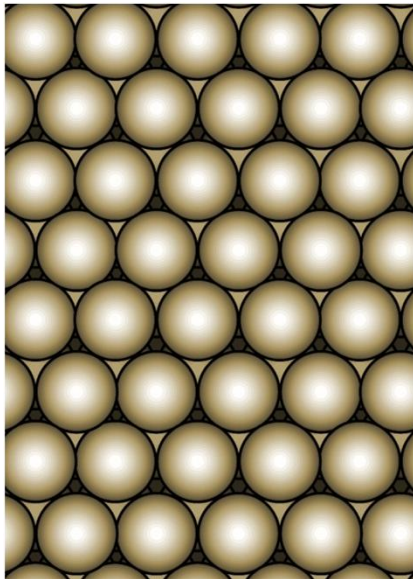
$$\text{površina} = \sqrt{2} ah = \sqrt{3} a^2 = \sqrt{3} \left(\frac{4\sqrt{3}}{3} R \right)^2 = \frac{16\sqrt{3}}{3} R^2$$

$$\text{Površinska gustina} = \frac{\text{atoma}}{\text{2D jedinična ćel}} = \frac{1}{\frac{16\sqrt{3}}{3} R^2} = 7.0 \frac{\text{atoma}}{\text{nm}^2}$$

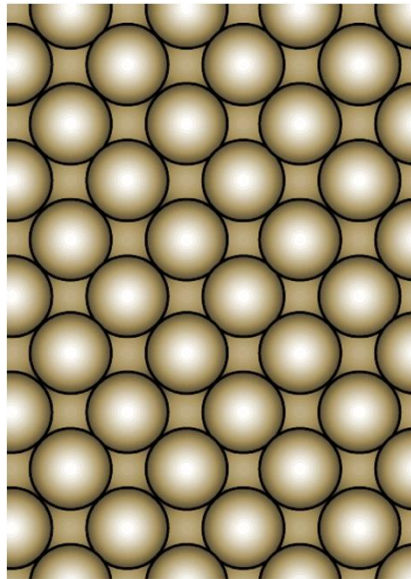
$$0.70 \times 10^{19} \frac{\text{atoma}}{\text{m}^2}$$

(111) , (100) , (110) FCC kristala

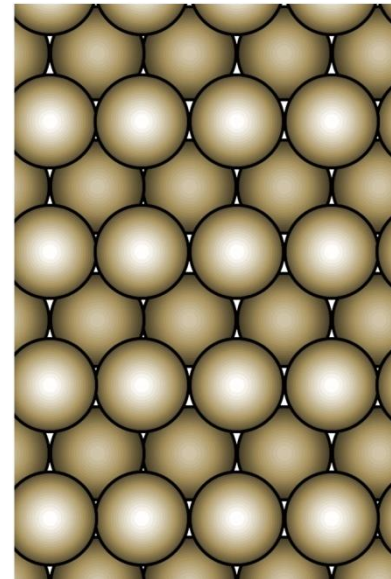
(111)



(100)



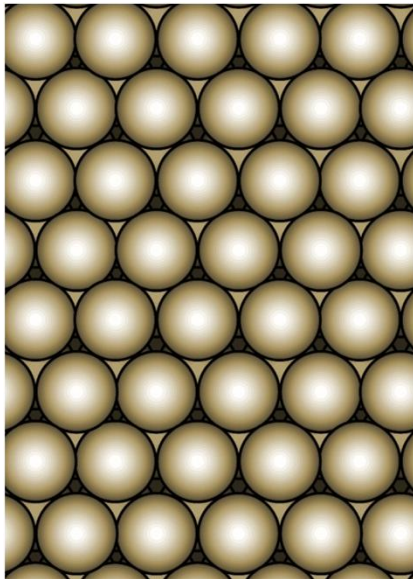
(110)



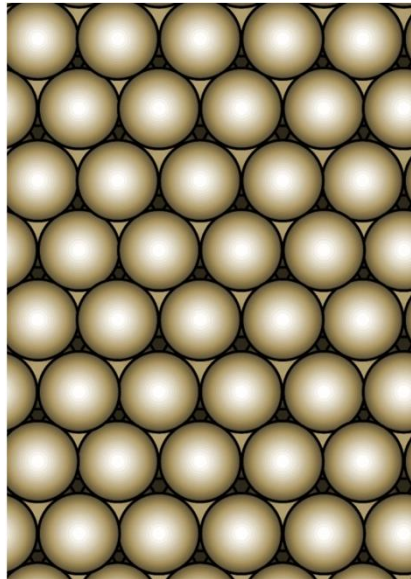
Idealne površine

Gusto pakovne površine FCC, BCC, HCP kristala imaju približno heksagonalni raspored atoma

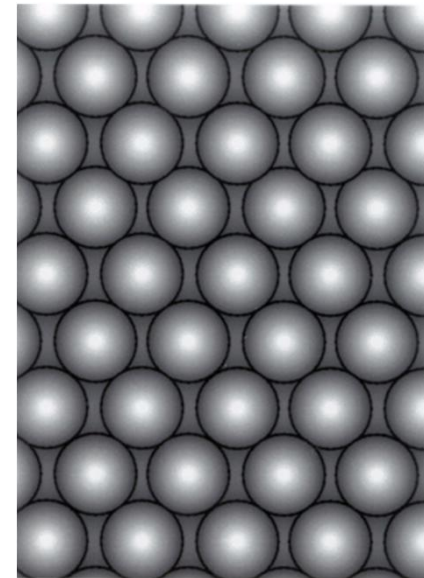
FCC (111)



HCP (001)

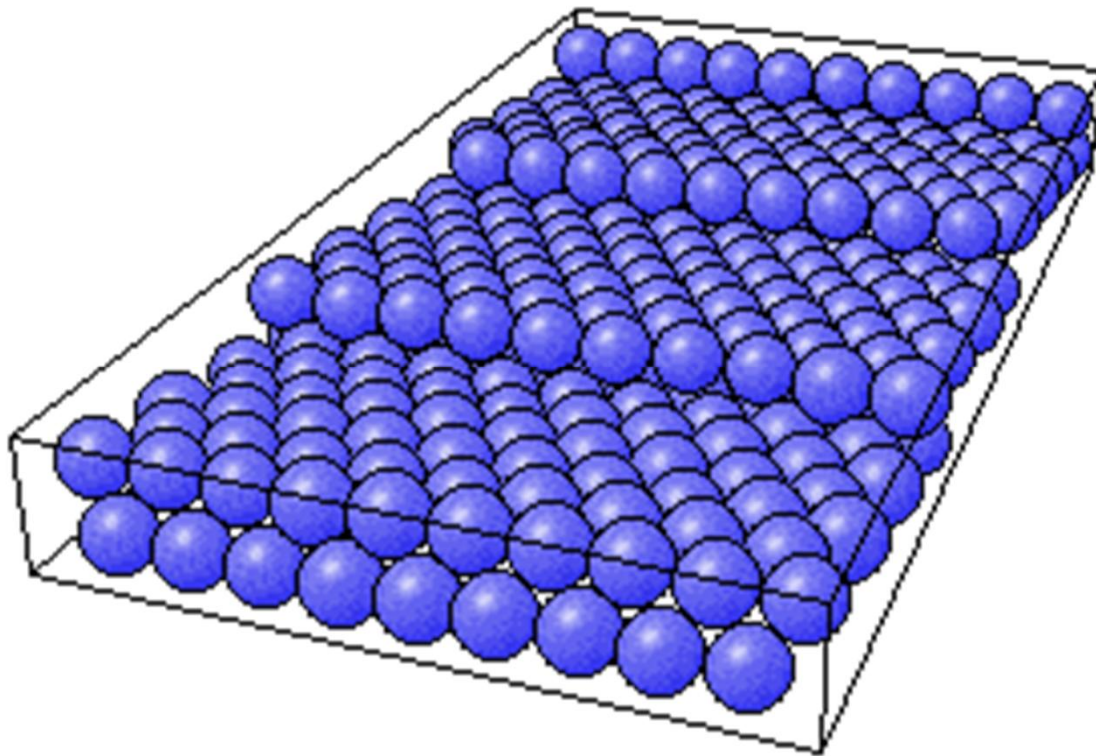


BCC (110)



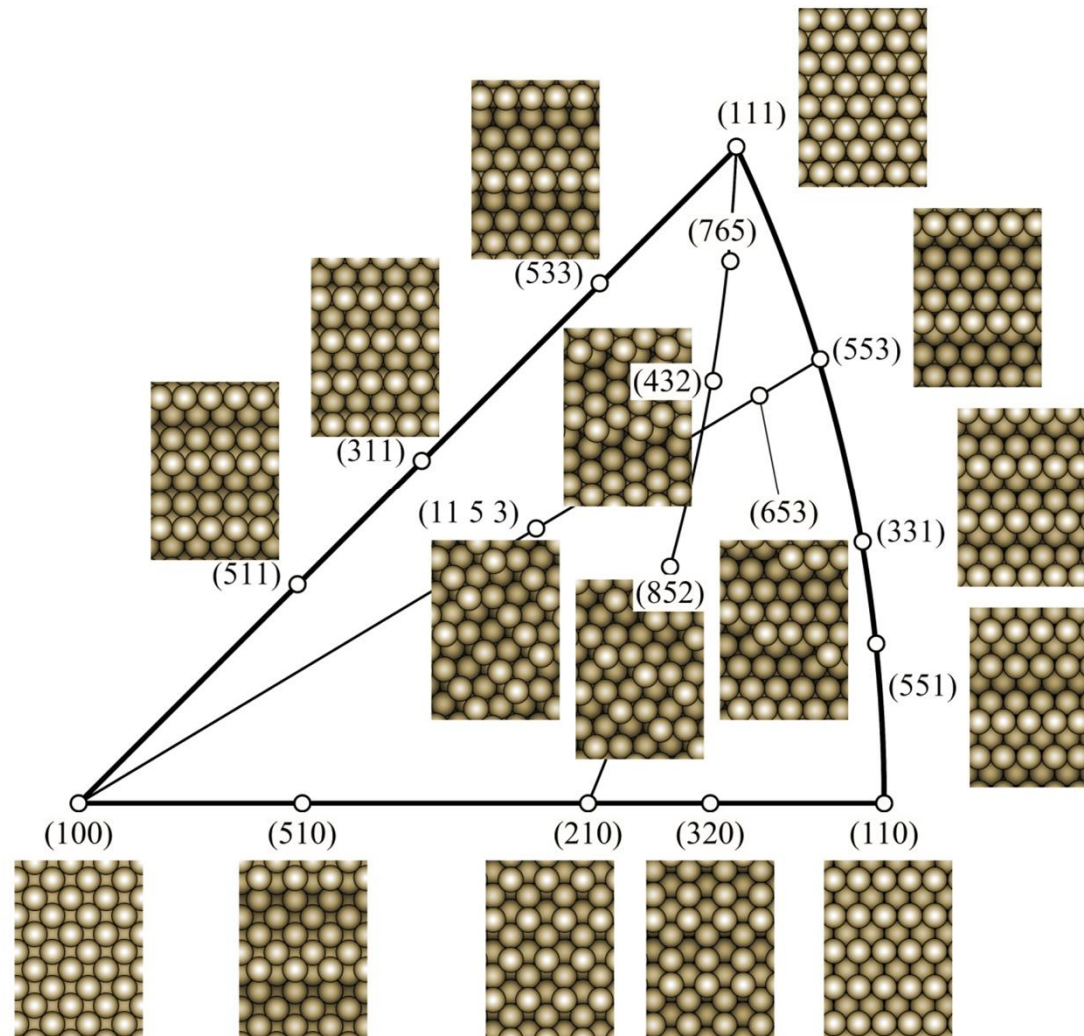
Površine visokih Milerovih indeksa:

Terasa + stepenik

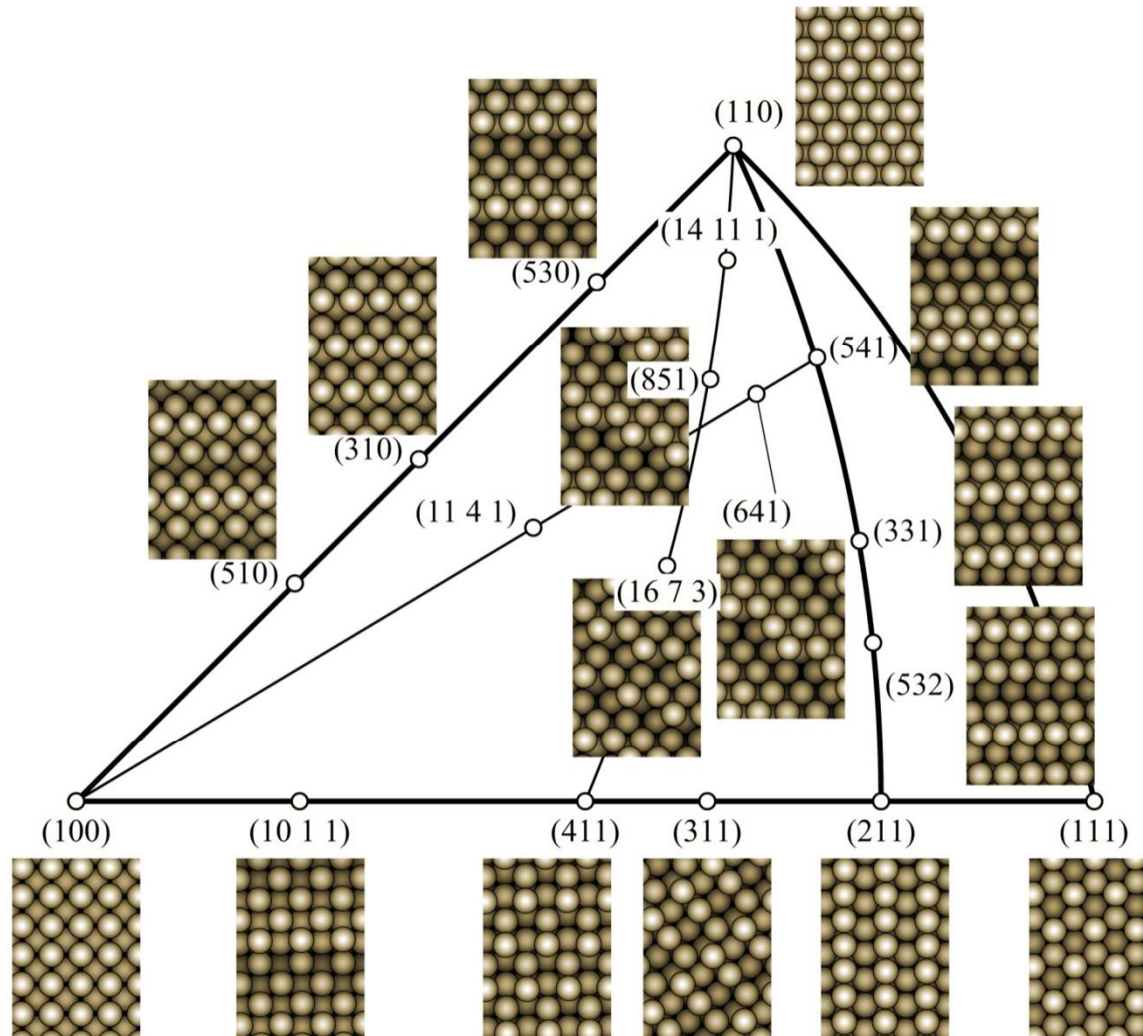


fcc(775)

Opšta slika FCC



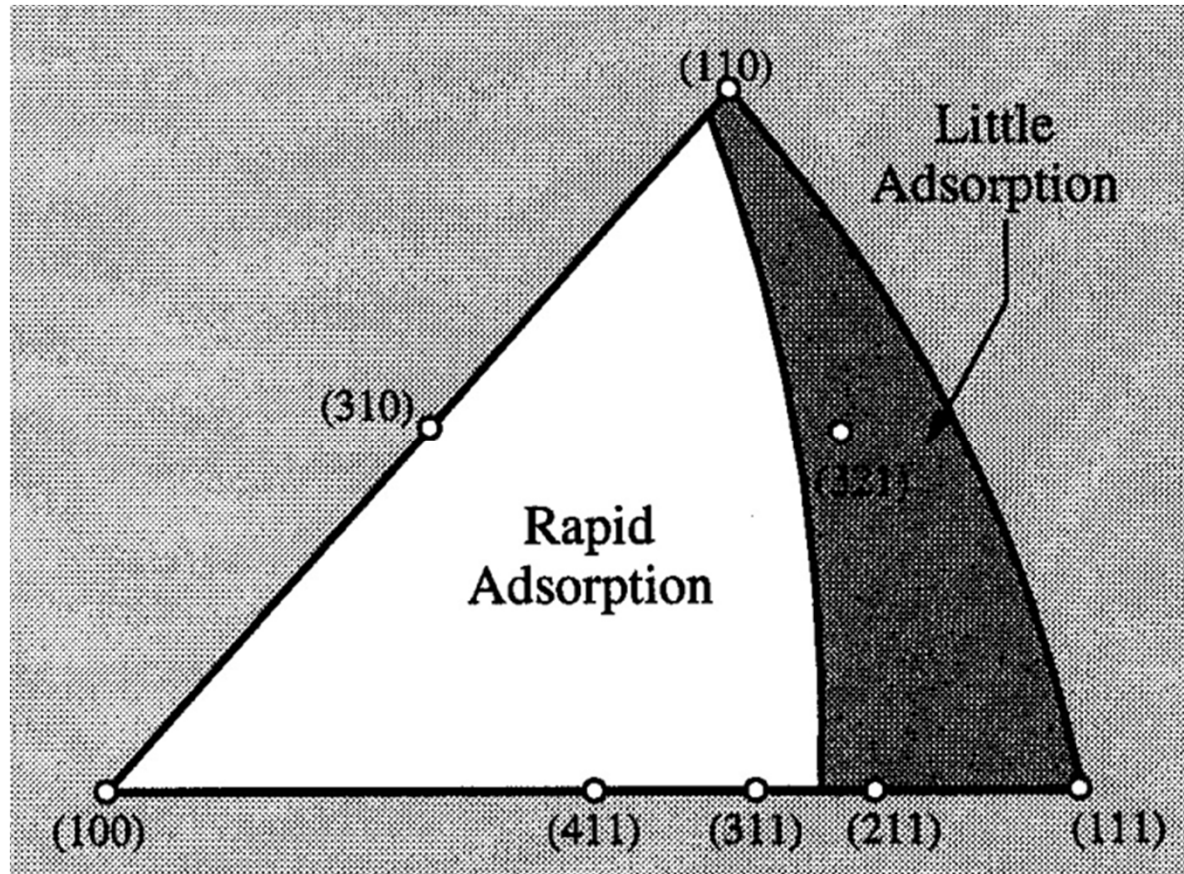
Opšta slika BCC (slično kao FCC)



$$\text{BCC (LMN)} \cong \text{FCC (L, M+N, M-N)}$$

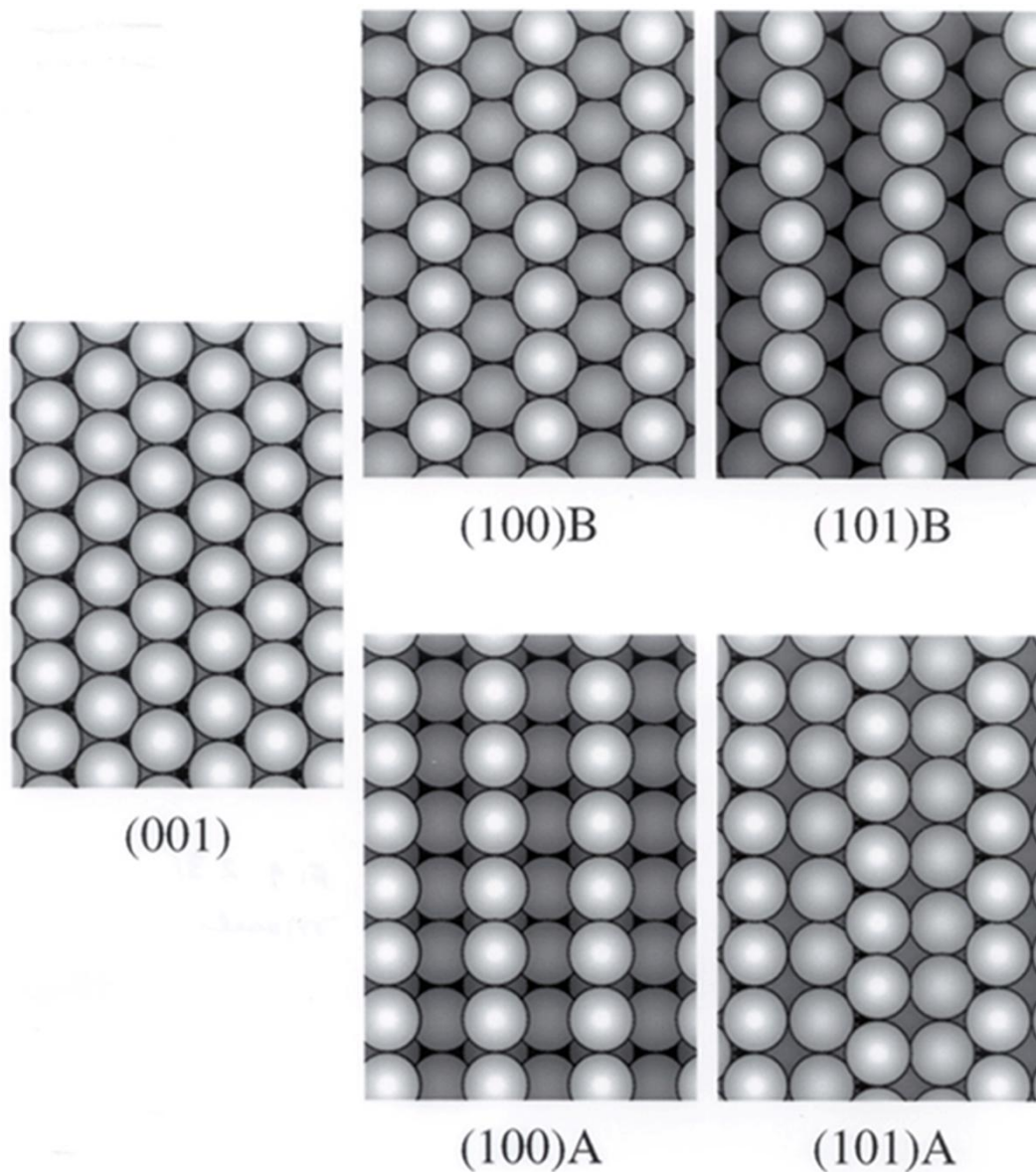
Reaktivnost zavisi od orijentacije površine

N_2 na W(hkl)



The rate of adsorption of nitrogen on tungsten as a function of the position of the plane within the stereographic triangle. (Data of Ehrlich and Hudda [1963], Delchar and Ehrlich [1965], and Adams and Germer [1971].)

HCP je malo drugačija



Rekonstrukcija i relaksacija površine

Idealna površina je samo aproksimacija

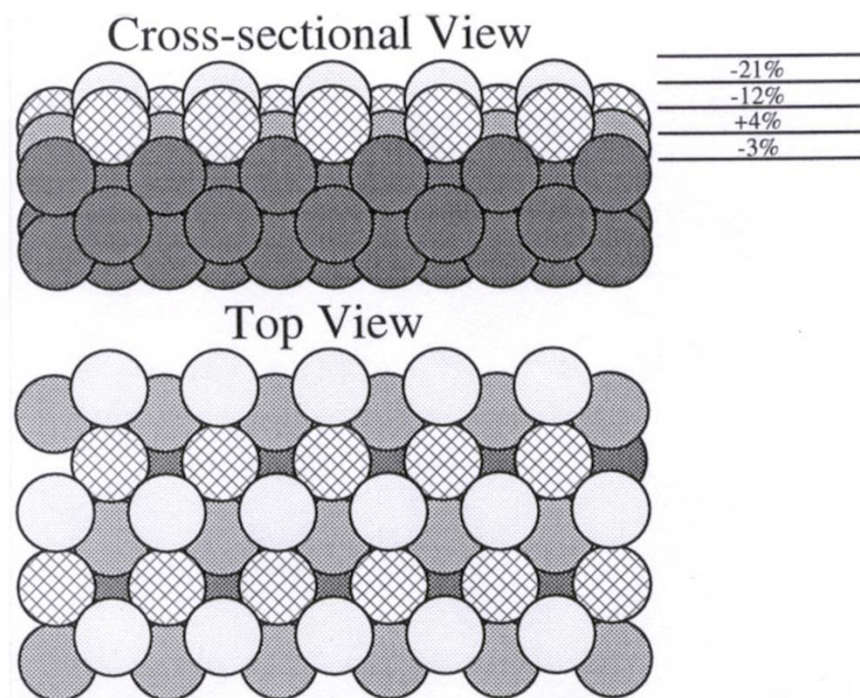
Dva tipa strukturnih promena: relaksacija i rekonstrukcija

Kod relaksacije promene su male, periodika ćelije nije promenjena

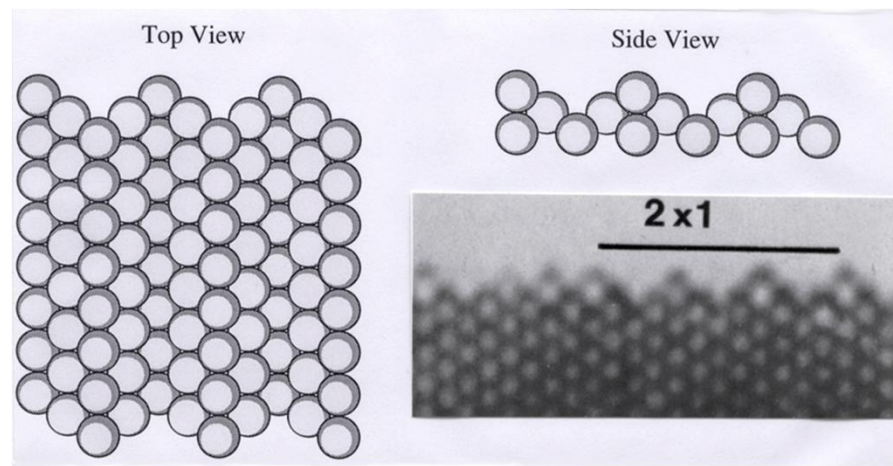
Kod rekonstrukcije velike strukturne promene, promena periodike jedinične ćelije površine u odnosu na dubinu materijala, izraženije kod kovalentnih kristala

Može biti indukovana adsorbatom

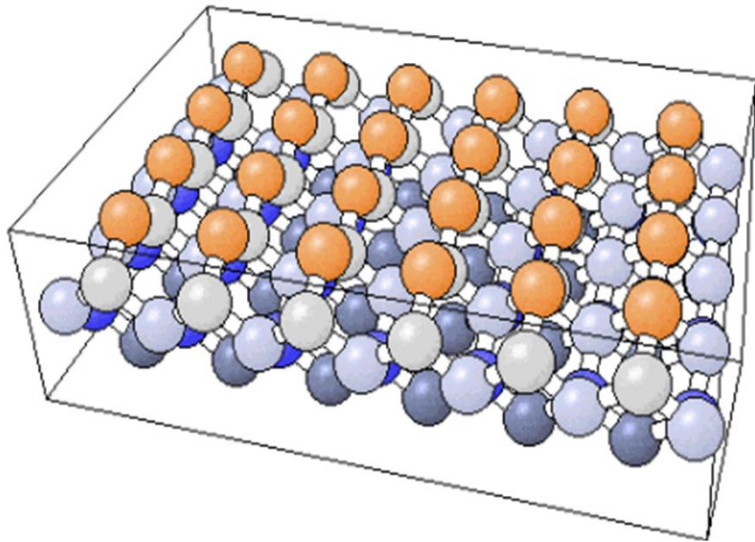
Relaksacija: Obično opada rastojanje između površinskih slojeva



Rekonstrukcija: preraspodela atoma da se površina oslobodi nezasićenih površinskih veza

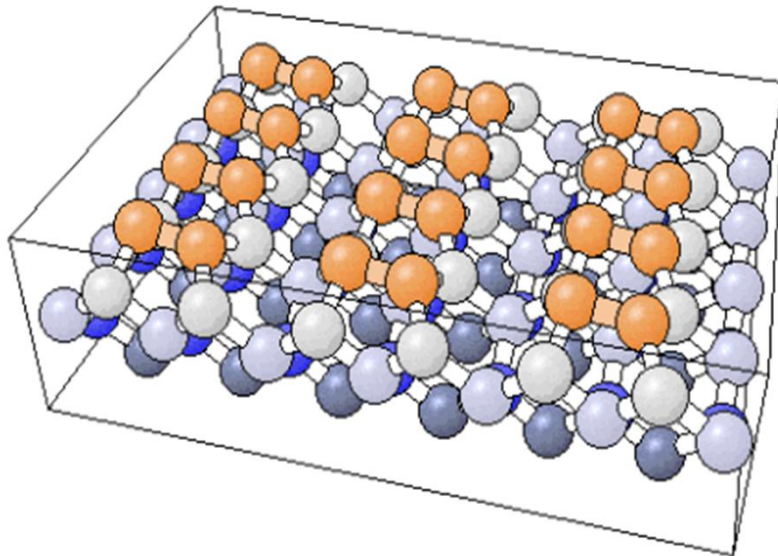


Si(100)-(2x1)



A. Unreconstructed Si(100)-(1x1) surface.

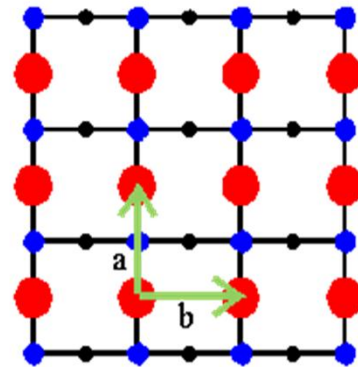
The Si atoms of the topmost layer are highlighted in orange; these atoms are bonded to only two other Si atoms, both of which are in the second layer (shaded grey).



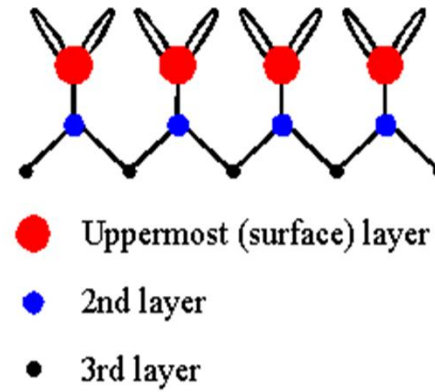
B. Reconstructed Si(100)-(2x1) surface.

The Si atoms of the topmost layer form a covalent bond with an adjacent surface atom; they are thus drawn together as pairs; they are said to form "*dimers*".

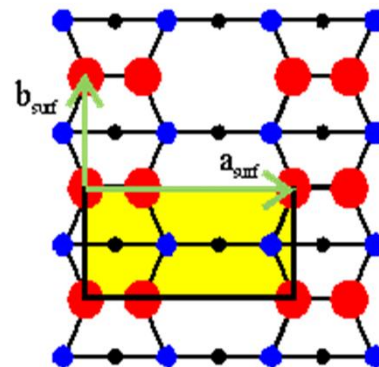
(a) UNRECONSTRUCTED Si(100)
(TOP VIEW)



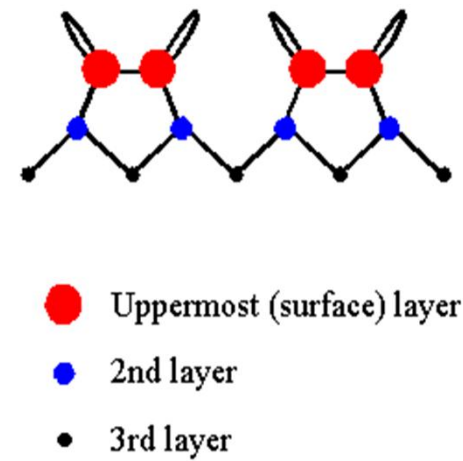
(b) UNRECONSTRUCTED Si(100)
(SIDE VIEW)

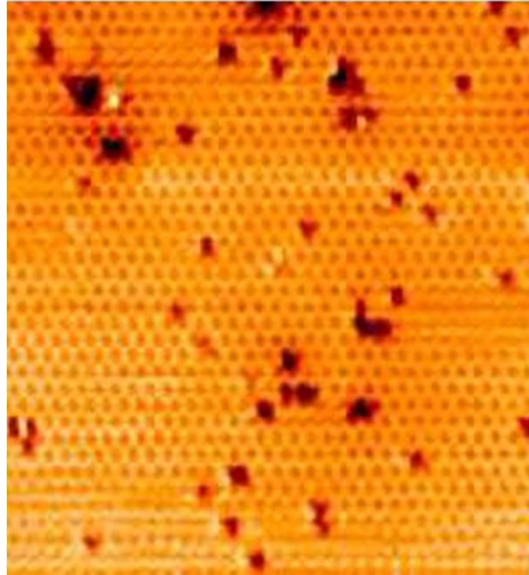


(a) RECONSTRUCTED Si(100)
(TOP VIEW)



(b) RECONSTRUCTED Si(100)
(SIDE VIEW)





Si(100) c(2x4) imaged at T = 120 K. At temperatures < 150 K the dimer row reconstruction of Si(100) is replaced by the honeycomb pattern of the c(2x4)-reconstruction (2nd order phase transition $(2\times 1) \leftrightarrow c(2\times 4)$). (20 nm x 20 nm)

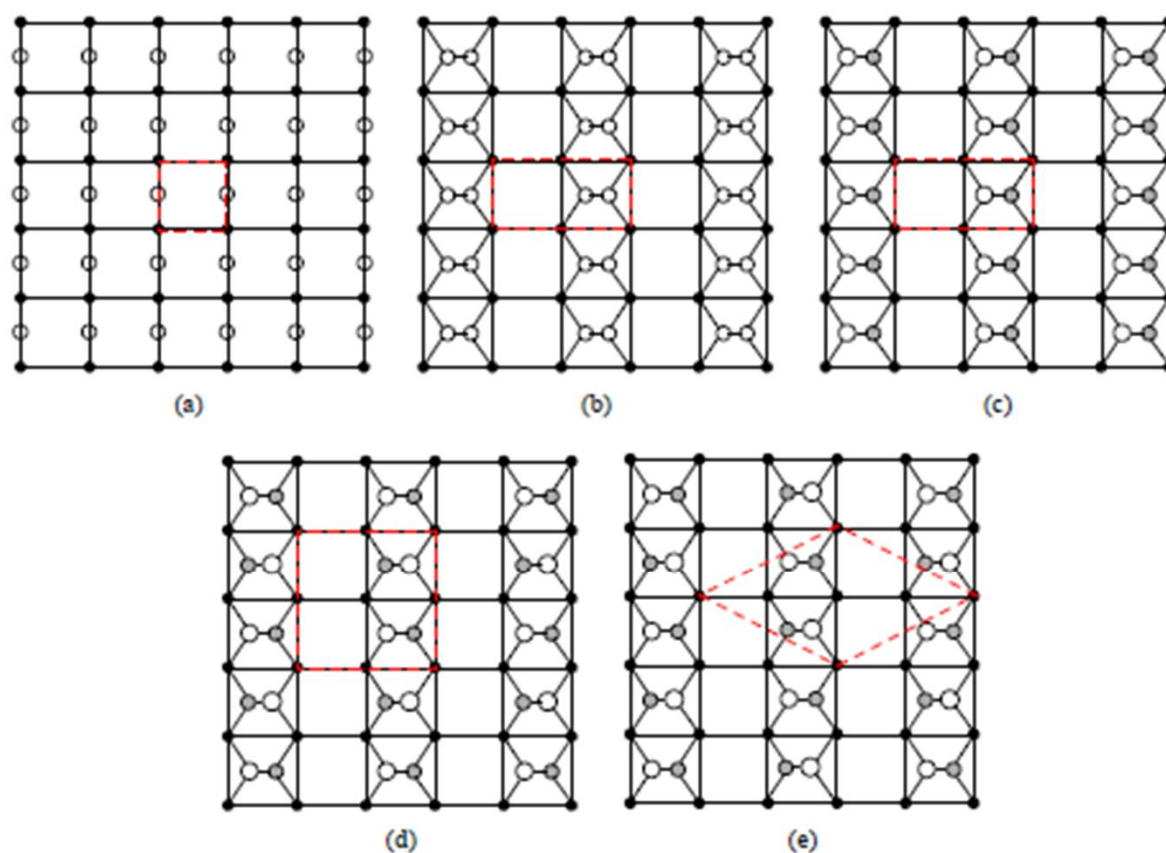


Fig. 4.1: Top view of different unit cells at the (001) surface for which we have calculated the surface energy. White circles show atoms in the surface layer and black circles represent atoms in the second layer but big white and small gray circles are used to show upward and downward buckled dimer atoms on the surface, respectively. The non-reconstructed surface (a), the (2×1) symmetric dimer reconstruction (b), the $p(2 \times 1)$ buckled dimer reconstruction (c), the $p(2 \times 2)$ alternating buckled dimer reconstruction (d), the $c(4 \times 2)$ reconstruction (e).

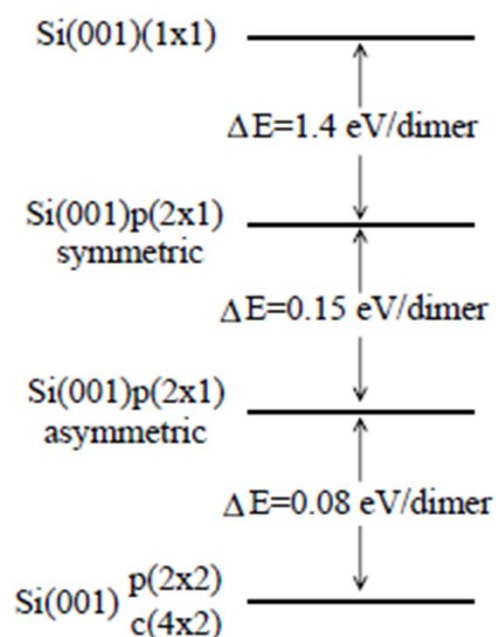


Fig. 4.5: Calculated energy difference between all possible surface reconstructions of the Si(001) surface.

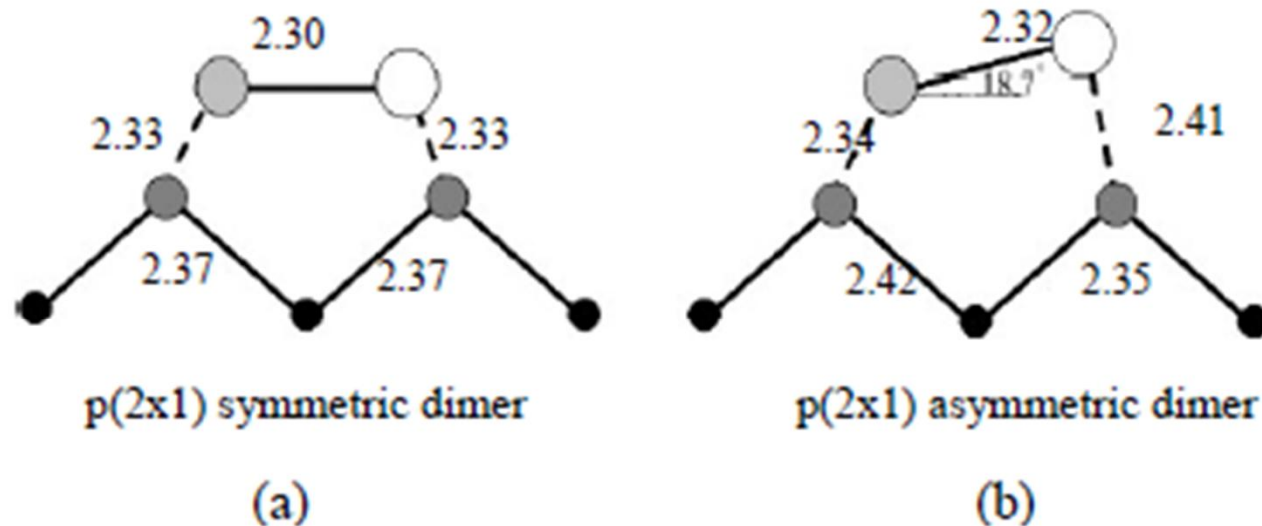
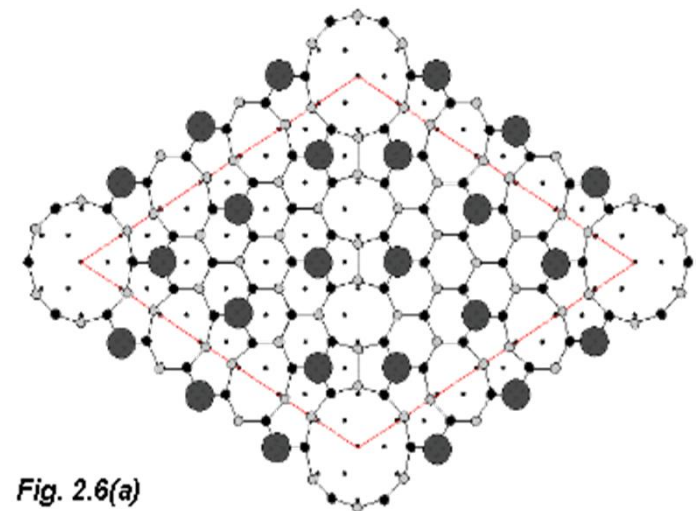
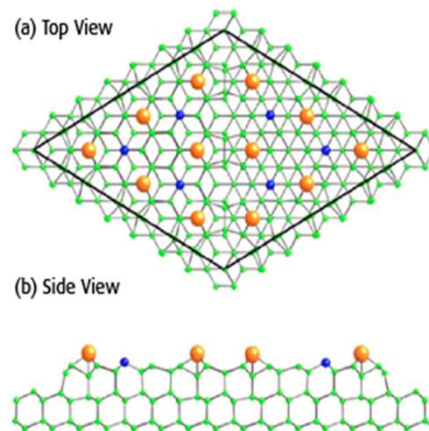
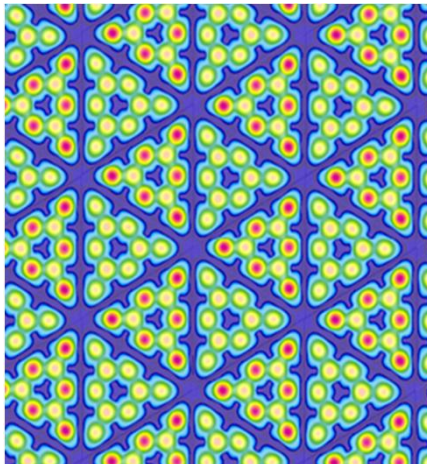
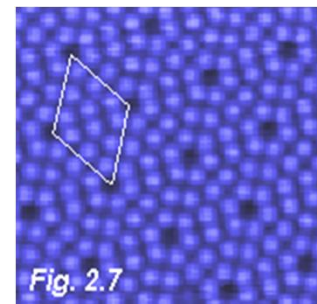
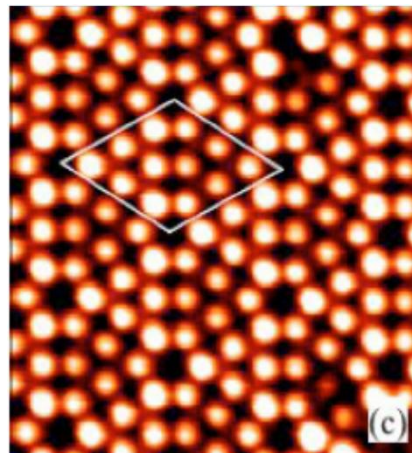
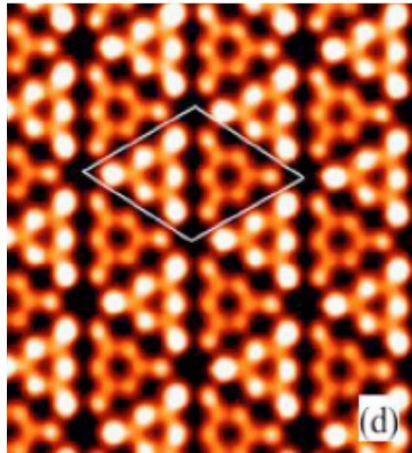


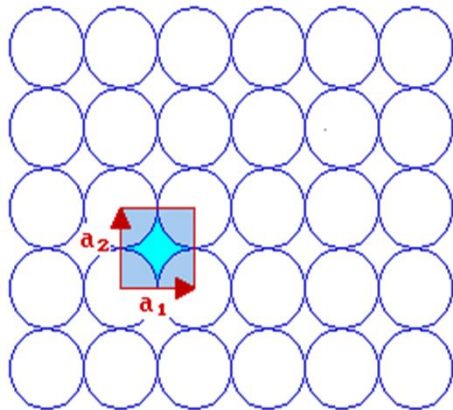
Fig. 4.2: Bond length of symmetric dimer structure (a), the bond length and the angle of the buckled dimer structure (b).

Si(111)-(7x7)

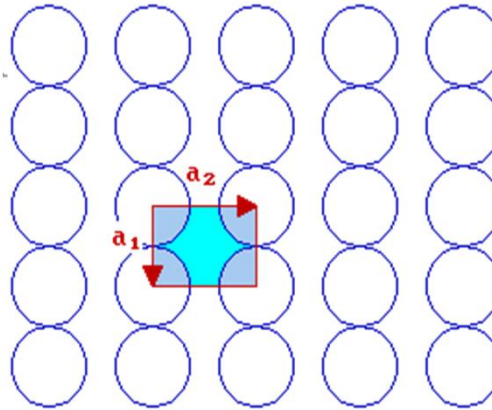


Wood-ova notacija: površinske strukture

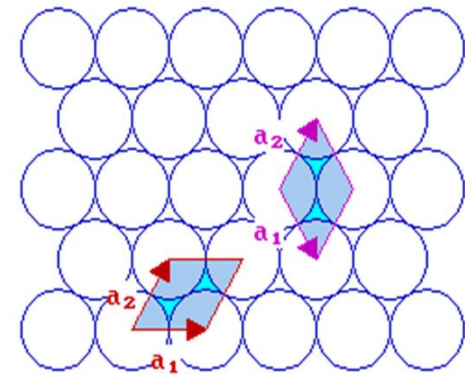
fcc (100) face

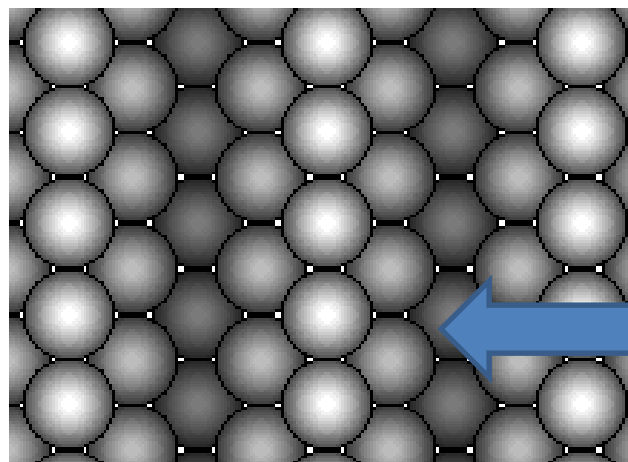
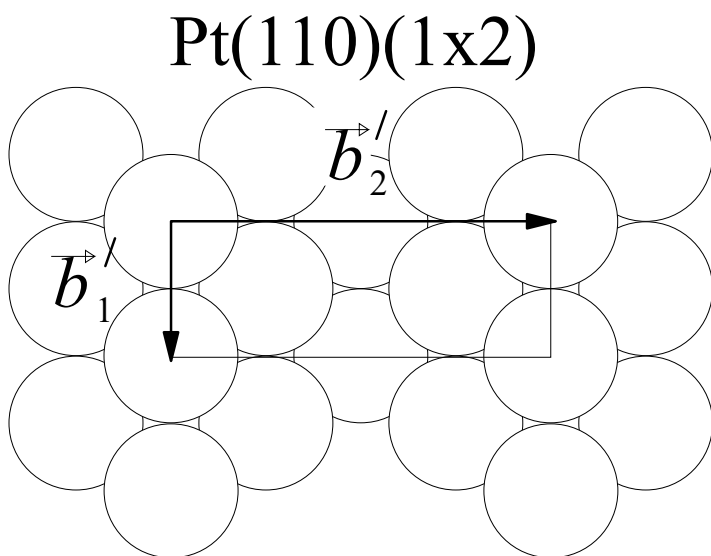
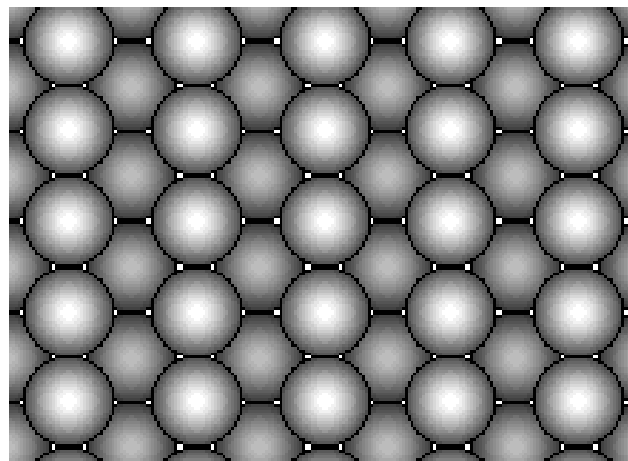
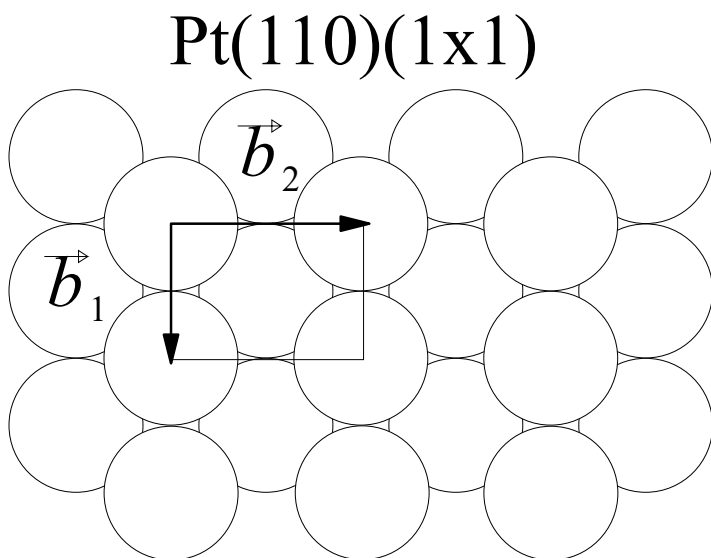


fcc (110) face



fcc (111) face





Pt(110)(1x2)

Lokalni
heksagonalni
raspored