Fizičkohemijski aspekti nauke o materijalima

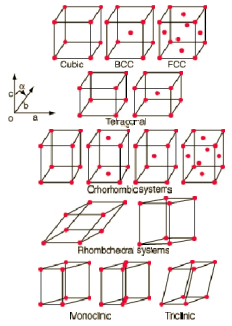
Deo 1

Igor Pašti

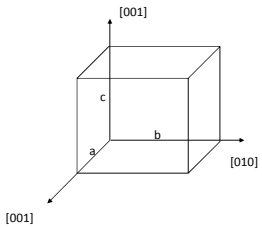
Sadržaj 1.1.

- Struktura kristala
- Elektronska struktura čvrstih materijala

7 sistema 14 Braveovih rešetki



Milerovi indeksi (hkl):



Pravci: [hkl]
Porodice pravaca: <hkl>
Ravni: (hkl)
Porodice ravni: {hkl}

Da bi se identifikovale ravni:
Korak 1 : identifikovati preseke na x- , y- i z- osama.
Korak 2 : Odrediti preseke u frakcionim koordinatama
Korak 3 : Uzeti recipročne vrednosti frakcionih koordinata odsečaka

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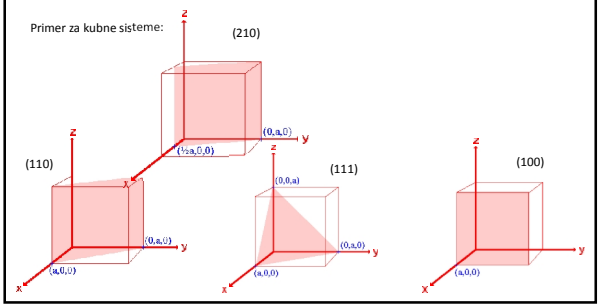
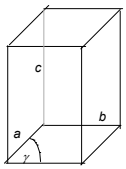
Primer za kubne sisteme:

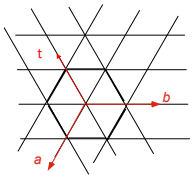


Hexagonalni sistemi



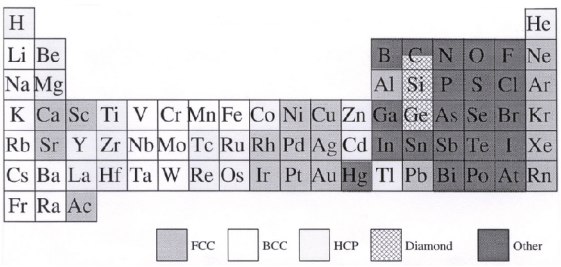
a = b, c
□= 120°

label 'low-index' planes parallel to c axis:



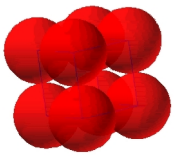
4 indeksa (Weberovi simboli)
(a b t c)
a + b + t = 0

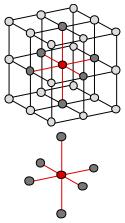
Periodni sistem



Jednostavna kubna struktura
Simple Cubic Structure (SC)

- Retka zbog male gustine pakovanja (samo Po ima ovu strukturu)
- Pravci gustog pakovanja su ivice kocke.
- koordinacioni # = 6
  (# broj najbližih suseda)





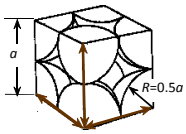
Broj atoma u ćeliji?

Faktor pakovanja atoma
Atomic Packing Factor (APF)

$$APF = \frac{\text{Zapremina atom u jediničnoj ćeliji*}}{\text{Zapremina jedinične ćelije}}$$

*pretpostavlja čvrste sfere

- APF za SCC= 0.52



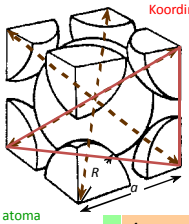
Pravci gustog pakovanja
sadrži 8 x 1/8 =
1 atom/jedinična ćelija

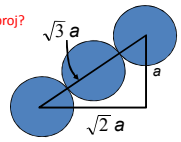
$$APF = \frac{\text{Atom}}{\text{Jedinična ćelija}} \cdot \frac{\text{zapremina atom}}{\text{zapremina Jedinična ćelija}} = \frac{1 \cdot \frac{4}{3}\pi (0.5a)^3}{a^3}$$

APF za BCC

- APF = 0.68

Koordinacioni broj?





Pravci gustog pakovanja su dijagonale kocke:

Dužina = $4R = \sqrt{3}\,a$

$$APF = \frac{\text{atoma}}{\text{Jedinična ćelija}} \cdot \frac{\text{zapremina}}{\text{atom}} \Big/ \frac{\text{zapremina}}{\text{Jedinična ćelija}}$$

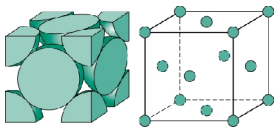
$$APF = \frac{2 \cdot \frac{4}{3}\pi \left(\frac{\sqrt{3}\,a}{4}\right)^3}{a^3}$$

Površinski centrirana kubna rešetka (FCC)

- Atomi se dodiruju duž dijagonala strana kocke.

Al, Cu, Au, Pb, Ni, Pt, Ag

- Koordinacioni # = 12

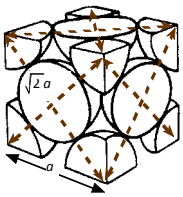


4 atoma/jedinična ćelija: 6 strana x 1/2 + 8 ćoškovi x 1/8

APF za FCC

- APF za FCC = 0.74

Maksimalni APF!



Pravci gustog pakovanja:

Dužina = $4R = \sqrt{2}\,a$

4 atoms/unit cell

$$APF = \frac{\text{atoma}}{\text{Jedinična ćelija}} \cdot \frac{\text{zapremina}}{\text{atom}} \Big/ \frac{\text{zapremina}}{\text{Jednična ćelija}}$$

$$APF = \frac{4 \cdot \frac{4}{3}\pi \left(\frac{\sqrt{2}\,a}{4}\right)^3}{a^3}$$

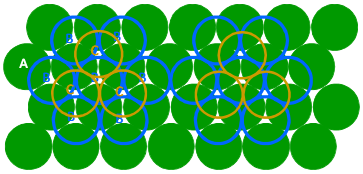
FCC slaganje

- ABCABC... Sekvenca duž 111 pravca
- 2D projekcija

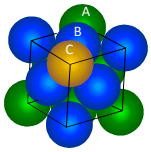
A mesta

B mesta

C mesta

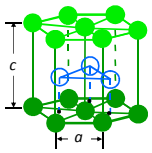


- jednična ćelija



Heksagonalna gusto pakovanje (HCP)

- ABAB... sekvenca
- 3D projakcija

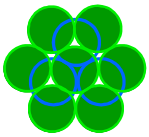


A mesta

B mesta

A mesta

- 2D projekcija



- koordinacioni # = 12
- APF = 0.74
- c/a = 1.633

6 atoma/jediničnoj ćeliji

Na primer: Cd, Mg, Ti, Zn

Teorijska gustina, □

$$\text{Gustina} = \rho = \frac{\text{Masa atoma u jediničnoj ćeliji}}{\text{Zapremina jedinične ćelije}}$$

$$\rho = \frac{n A}{V_C N_A}$$

n = broj atoma u jedničnoj ćeliji
A = atomska težina
V_C = zapremina jedinične ćelije= a^3 za kubne sisteme
N_A = Avogadrov broj
= 6.022 x 10^{23} atom/mol

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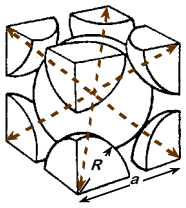
Teorijska gustina, ρ



- Primer: Cr (BCC)
  - A = 52.00 g/mol
  - R = 0.125 nm
  - n = 2 atoma u jediničnoj ćeliji

$a = 4R/\sqrt{3} = 0.2887$ nm

$$\rho = \frac{\text{atoma}/\text{Jedinična ćelija} \times g/mol}{\text{zapremina}/\text{Jedinična ćelija} \times \text{atom}/mol} = \frac{2 \times 52.00}{a^3 \times 6.022 \times 10^{23}}$$

$\rho_{teorijska}$ = 7.18 g/cm³

$\rho_{stvarna}$ = 7.19 g/cm³

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Gustine različitih klasa materijala

Uopšteno

ρ metali > ρ keramike > ρ polimeri

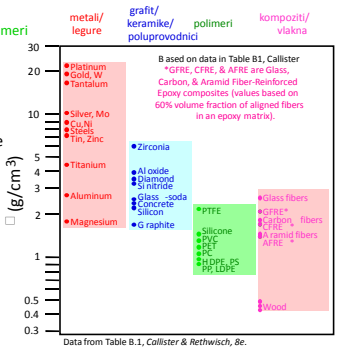
Zašto?

Metali imaju:
- gusto pakovanje (metalna veza)
- često velike atomske mase

Keramike imaju...
- manje gusta pakovanja
- lakše elemnte

Polimeri imaju...
- malu gustinu pakovanja (često amorfni)
- lake elemente (C,H,O)

Kompoziti imaju...
- nešto između



Data from Table B.1, *Callister & Rethwisch, 8e.*

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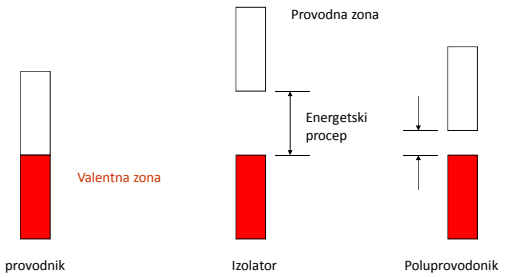
Elektronska struktura čvrstih metala

- Zonska teorija
- Elektronski provodnici: uglavnom metali
- Izolatori: uglavnom nemetalni materijali
- Poluprovodnici (metaloidi)

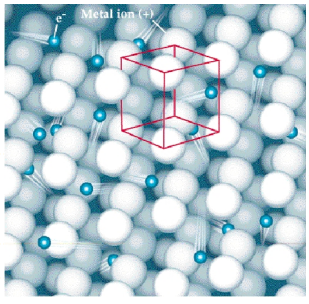
Čvrsti materijali



Vezivanje u metalima

- Niz pozitivnih jona okružen delokalizovanim valentnim elektronima
  - Dobri elektronski provodnici zbog mobilnosti delokalizovanih valentnih elektrona
  - Dobri toplotni provodnici

Vezivanje u metalima



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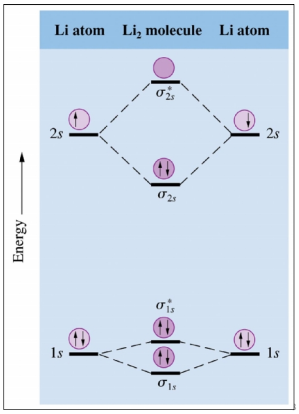
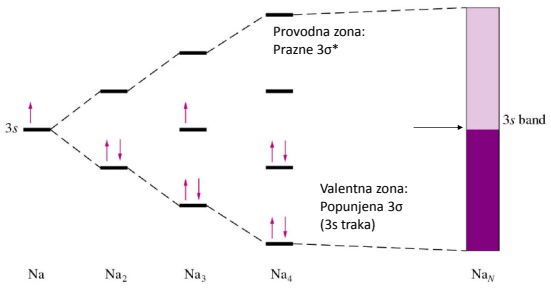
Vezivanje u metalima

- Energetski nivoi formiraju energetske zone ili trake
- Kada se ekscitiraju elektroni prelaze na slobodne nivoe u energetskoj zoni
- S obzirom da nema energetskog procepa ovo zahteva vrlo malo energije

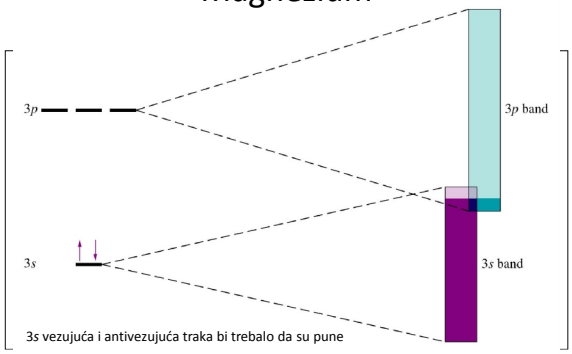
Vezivanje u metalima Li prema MO teoriji



Na prema zonskoj teoriji

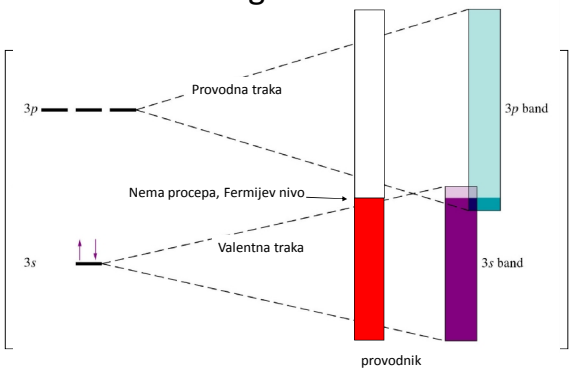


Magnezium

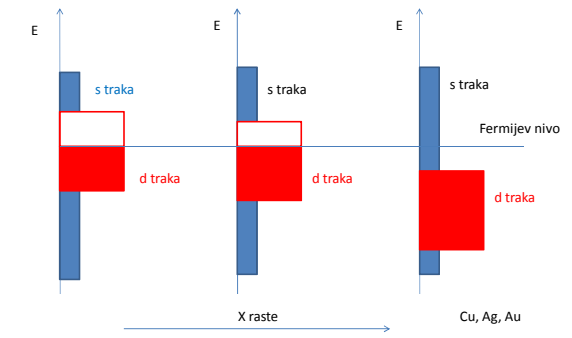


3s vezujuća i antivezujuća traka bi trebalo da su pune

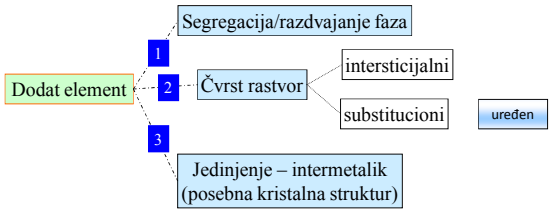
Magnezium



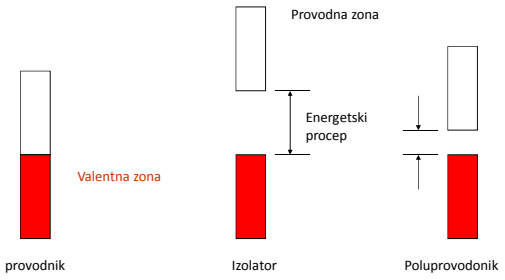
Prelazni metali $(n-1)d^x ns^1$



Dodatak legirajućeg elementa



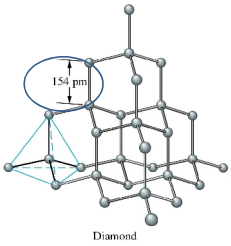
Čvrsti materijali



Alotropi ugljenika – dijamant vs. grafit

- Dijamant: visoka toplotna provodljivost, ekstremno čvrst, izolator
- Grafit: visoka toplotna provodljivost, provodnik

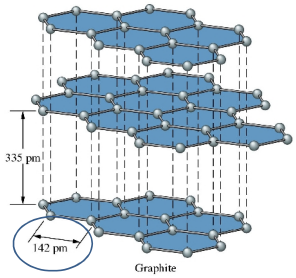
Sruktura dijamanta



Diamond

- **3D struktura, jednostruke veze, sp^3 hibridizacija**.
- Zašto provodi toplotu?
  - Kod metala pokretni elektroni nose višak kinetičke energije.
  - Dijamant je izolator bez pokretnih naelektrisanja.
  - Toplota se provodi preko vibracija rešetke
- 4 puta bolji toplotni provodnik od bakra!

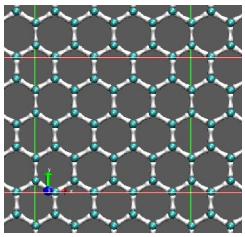
Struktura grafita



Graphite

Grafit

- **Grafit ima slojevitu strukturu**.
- Grafenski sloj – sp^2 hibiridizacija, delokalizovani elektroni, slojevi povezani slabim VdW vezama
- Jedini kovalentni kristal koji provodi struju



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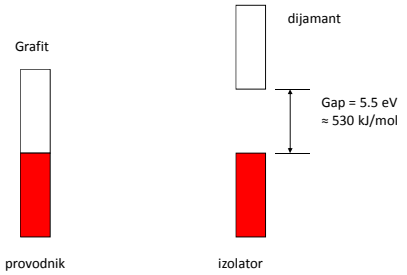
Energetske zone



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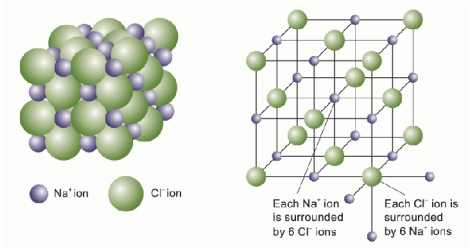
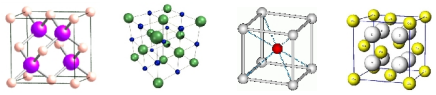
Jonski kristali – tipični primeri izolatora

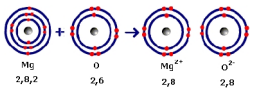


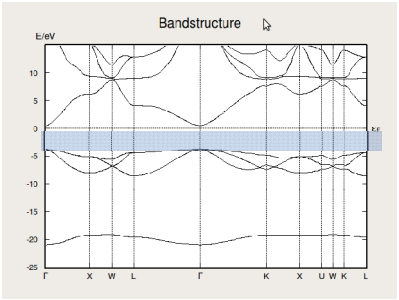
Na^+ popunjava praznine između Cl^-

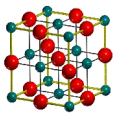
Interstitial site	Tetraedarska	Oktaedarska	Kubna	Kubna
Coordination	4 : 4	6 : 6	8 : 8	8:4
r^+/r^-	0.225 – 0.414	0.414 – 0.732	0.732 – 1.000	0.732 – 1.000
Examples	ZnS, most copper(I) halides	Alkali metal halides except CsCl	CsCl, CsBr CsI, NH_4Cl	CaF_2, BaF_2, $BaCl_2$, SrF_2



MgO



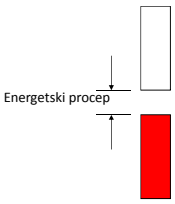




Čvrsti materijali - izolatori

Energetski procep kod poluprovodnika

dijamant 5.5 eV - izolator	
Si	1.1 eV
Ge	0.67 eV



poluprovodnik

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Poluprovodnici

- Metaloidi: poluprovodnički elementi
  - Niska električna provodljivost na sobnoj temperaturi
  - Provodljivost raste sa temperaturom
- Energetski procep “osrednji”
- Dopiranjem dramatično raste provodljivost

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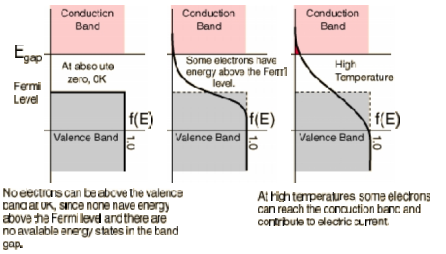
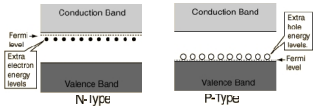
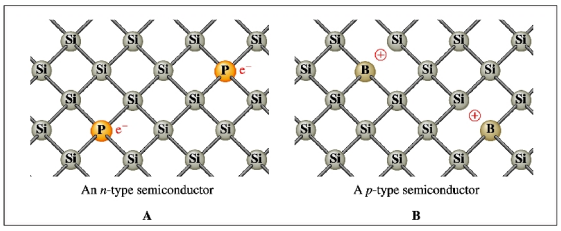


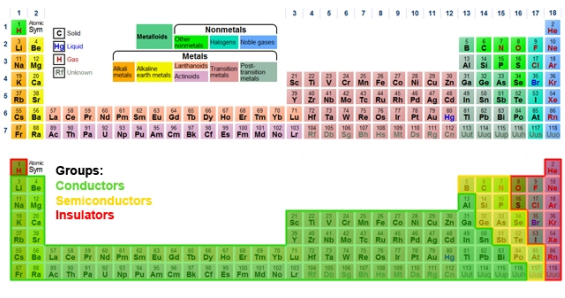
Dopirani poluprovodnik



DOPIRANJE SILICIJUMA



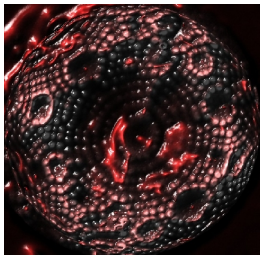
41



Površina

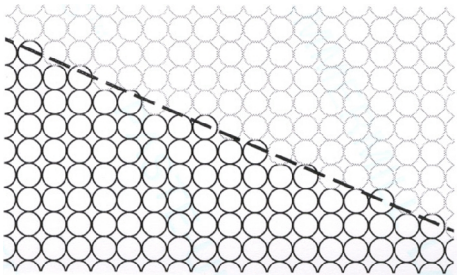
IDEJA: Kada se formira površina raspored atoma na površini ostaje sličan kao u kristalu

SADRŽAJ 1.2.
Čvrsta površina
- Kristalna struktura
- Elektronska struktura
- Rekonstrukcija i relaksacija



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

Formiranje površine



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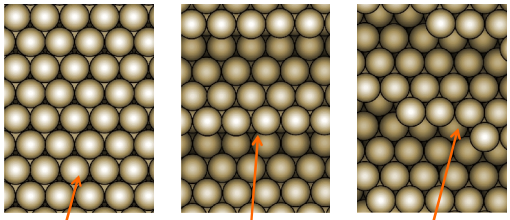
Neke od karakterističnih lokalnih struktura na površinama



Notacija površinskih struktura

Ideja:

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

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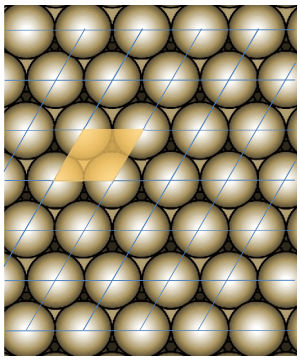
Jedinična površinska ćelija



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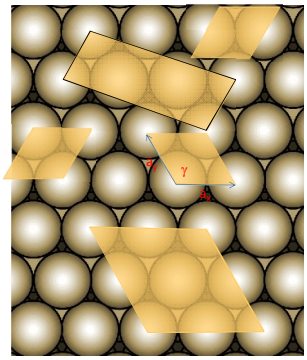
Izbor nije jedinstven



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2D Braveove rešetke

Ideja – klasifikovati jediničnu ćeliju prema simetriji

6 Braveovih rešetki u 2D

		Conventional	Axes of Conventional
Lattice	Axes of Primitive Cell	Cell	Cell
Oblique	$a_x \neq a_y$, $\gamma \neq 90^\circ$ or 120°	Parallelogram	$a_x \neq a_y$, $\gamma \neq 90^\circ$ or 120°
Centered rectangle	$a_x = a_y$, $\gamma \neq 90^\circ$ or 120°	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	$a_x = a_y^2$	90^0 square	$a_x = a_y$ x=90^0

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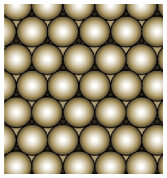
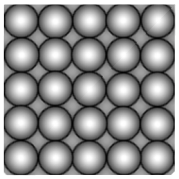
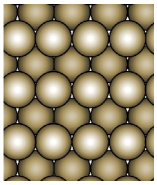
Šestougao



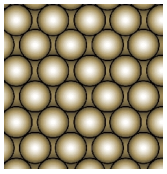
Kvadrat



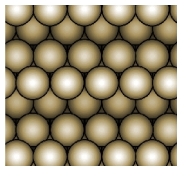
Pravougaonik



Centrirani pravougaonik

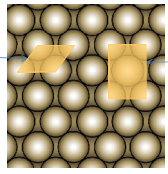


Pravougaonik



Centrirani pravougaonik

Primitivna ćelija



Konvencionalna jedinična ćelija

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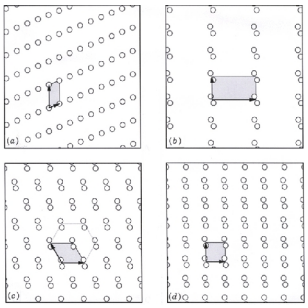
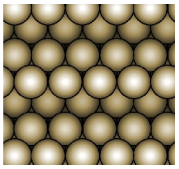
Jedinična ćelija + strukturni motiv





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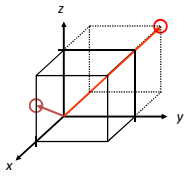
Kristalografski pravci



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, ½ => 2, 0, 1 => [201]

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

Familija pravaca <*uvw*>

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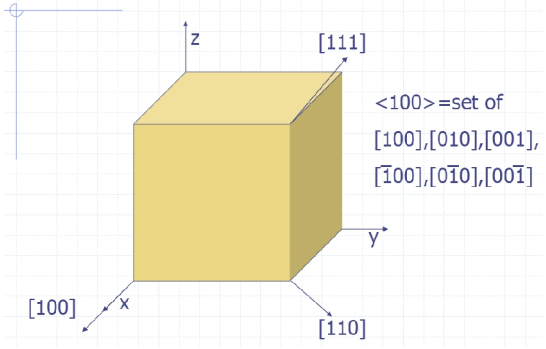
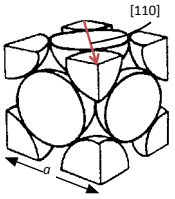
Miller indices: Directions



Linearna gustina

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



primer: linearna gustina Al u pravcu [110]

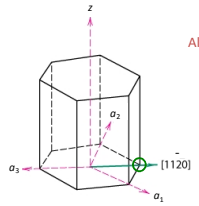
a = 0.405 nm

atoma

$$LD = \frac{2}{\sqrt{2}a} = 3.5\ \text{nm}^{-1}$$

dužina

HCP kristalograski pravci



Algoritam

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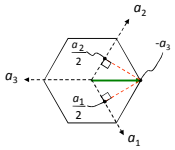
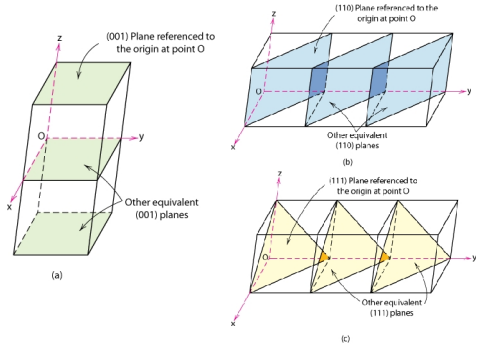
2. Pročitati projekcije u umnošku a, b i c
3. Podesiti na najmanje cele brojeve
4. dati u fomi [*uvw*]

Primer: ½, ½, -1, 0 => $[11\bar{2}0]$



Kristalografske ravni



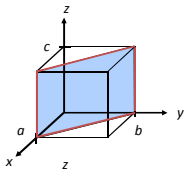
Kristalografske ravni

- Milerovi indeksi: kako se određuju?
- Sve paralelne ravni imaju iste Milerove indekse.

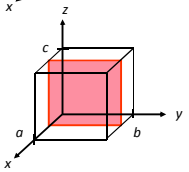
- Algoritam
  1. Očitati preseke ravni sa *a*, *b*, *c*
  2. Uzeti recipročne vrednosti odsečaka
  3. Redukovati na najmanje cele brojeve
  4. U zagrade, bez zareza (*hkl*)

Kristalografske ravni

Primer	*a*	*b*	*c*
1. Preseci	1	1	∞
2. Recipročno	1/1	1/1	1/∞
	1	1	0
3. Redukcija	1	1	0
4. Milerovi indeksi	(110)		



Primer	*a*	*b*	*c*
1. Preseci	1/2	∞	∞
2. Recipročno	1/½	1/∞	1/∞
	2	0	0
3. Redukcija	2	0	0
4. Milerovi indeksi	(200)		



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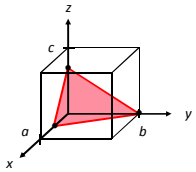
Kristalografske ravni

Primer	*a*	*b*	*c*
1. Preseci	1/2	1	3/4
2. Recipročno	1/½	1/1	1/¾
	2	1	4/3
3. Redukcija	6	3	4
4. Milerovi indeksi	(634)		

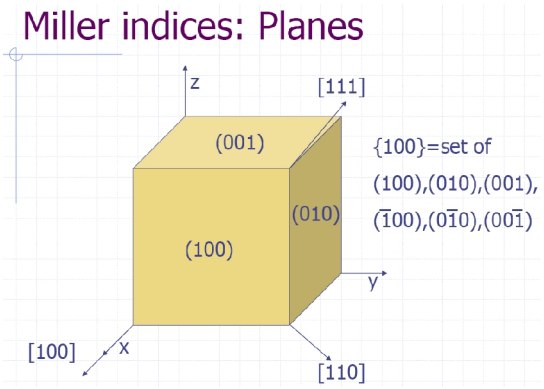


Porodica ravni {*hkl*}

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

60

Miller indices: Planes

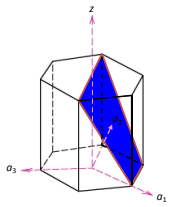


Heksagonalni sistem (HCP)

- Ista ideja

Primer	a_1	a_2	a_3	c
1. Preseci	1	∞	-1	1
2. Recipročno	1	1/∞	-1	1
	1	0	-1	1
3. Redukcija	1	0	-1	1

4. Indeksi $(10\bar{1}1)$

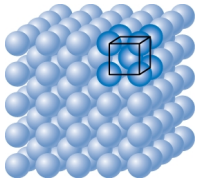


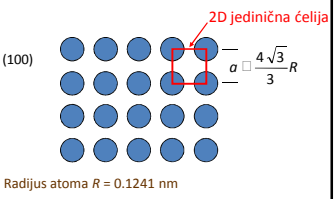
Površinska gustina

- Utiče na površinsku energiju
- Stabilnost površine
- Reaktivnost površine

Površinska gustina Fe(100)

T < 912ºC BCC struktura.



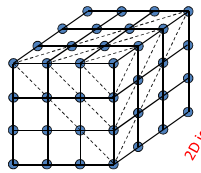


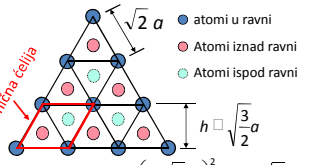
Radijus atoma R = 0.1241 nm

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

Površinska gustina Fe(111)

1 atom u ravni/ jedinična ćelija

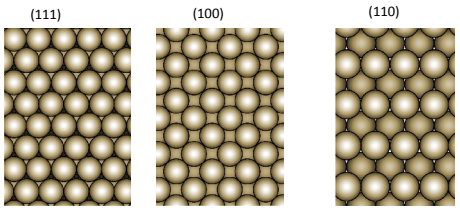




površina $= \sqrt{2}\,ah = \sqrt{3}\,a^2 = \sqrt{3}\left(\frac{4\sqrt{3}}{3}R\right)^2 = \frac{16\sqrt{3}}{3}R^2$

$$\text{Površinska gustina} = \frac{\text{atoma / 2D jediniča ćel}}{\text{površina / 2D jedinična ćelija}} = \frac{1}{\frac{16\sqrt{3}}{3}R^2} = 7.0 \frac{\text{atoma}}{\text{nm}^2} = 0.70 \times 10^{19} \frac{\text{atoma}}{\text{m}^2}$$

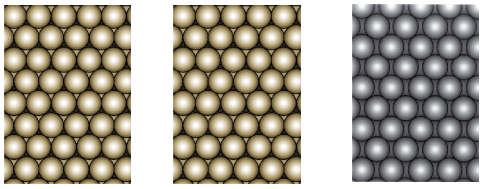
(111), (100), (110) FCC kristala



Idealne površine

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

FCC (111) HCP (001) BCC (110)



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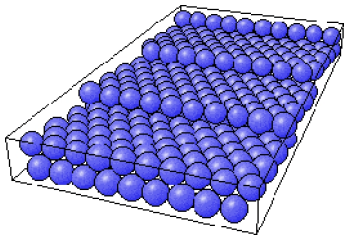
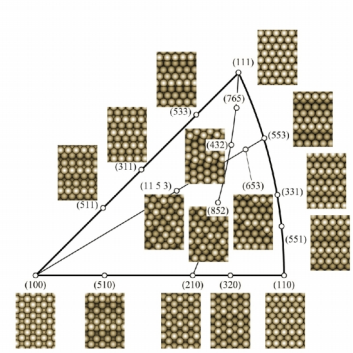
Površine visokih Milerovih indeksa:

Terasa + stepenik



fcc(775)

Opšta slika FCC



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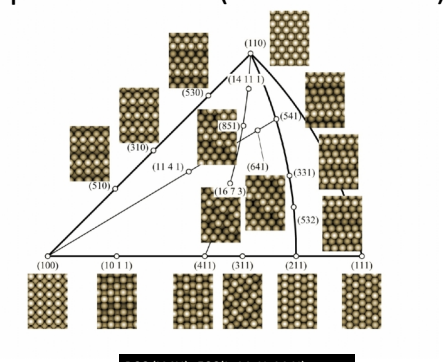
Opšta slika BCC (slično kao FCC)



BCC (LMN)≅FCC(L, M+N, M-N)

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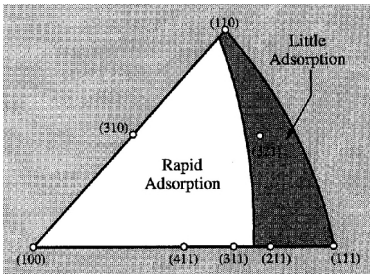
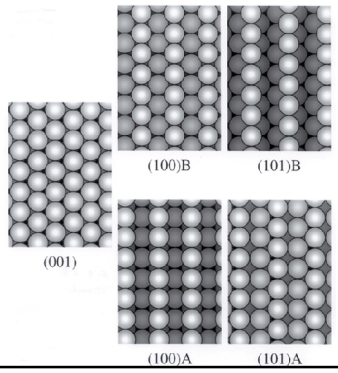
Reaktivnost zavisi od orijentacije površine

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



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Rekonstrukcija i relaksacija površine

Idealna površina je samo aproksimacija

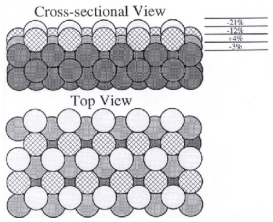
Dva tipa strukturnih promena: relaksacija i rekonstrukcija

Kod relaksacije promene su male, periodika ćelije nije promenjena

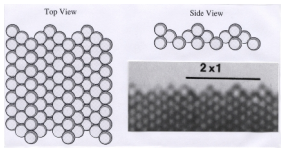
Kod rekonstrukcije velike strukturne promene, promena periodike jedinične ćelije površine u odnosu na dubinu materijala, izraženije kod kovalentnih kristala

Može biti indukovana adsorbatom

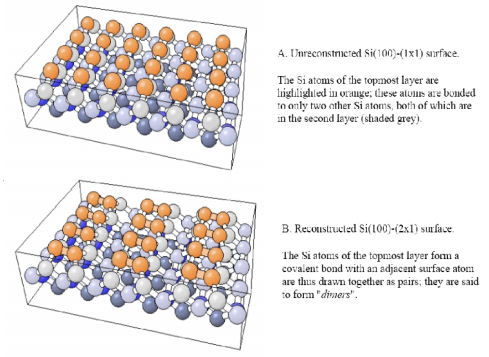
Relaksacija: Obično opada rastojanje između površinskih slojeva



Rekonstrukcija: preraspodela atoma da se površina oslobodi nezasićenih površinskih veza



Si(100)-(2x1)

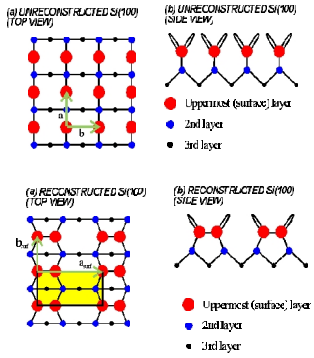


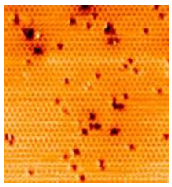
A. Unreconstructed Si(100)-(1x1) surface.

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 are thus drawn together as pairs; they are said to form "*dimers*".





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 (2x1)↔c(2x4)). (20 nm x 20 nm)

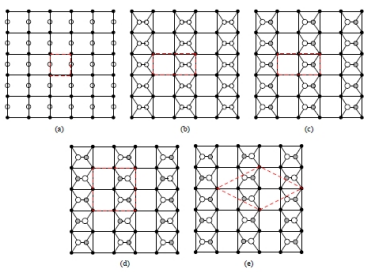


Fig. 4.1: Top view of different unit cells at the (001) surface for which we have calculated the surface energy. White circles show atoms in the surface layer and black circles represent atoms in the second layer but big white and small gray circles are used to show upward and downward buckled dimer 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).

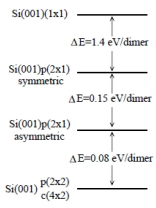
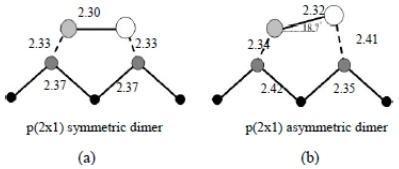


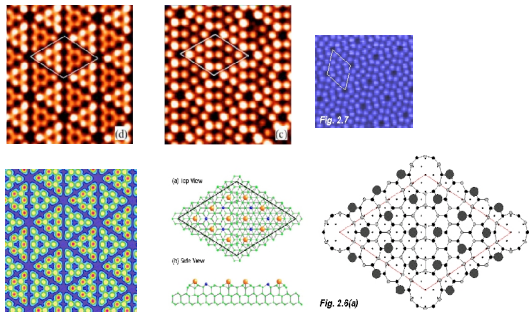
Fig. 4.5: Calculated energy difference between all possible surface reconstructions of the Si(001) surface.



p(2x1) symmetric dimer (a) p(2x1) asymmetric dimer (b)

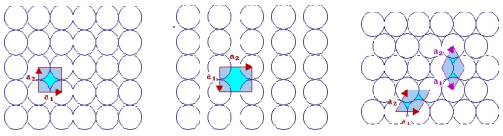
Fig. 4.2: Bond length of symmetric dimer structure (a), the bond length and the angle of the buckled dimer structure (b).

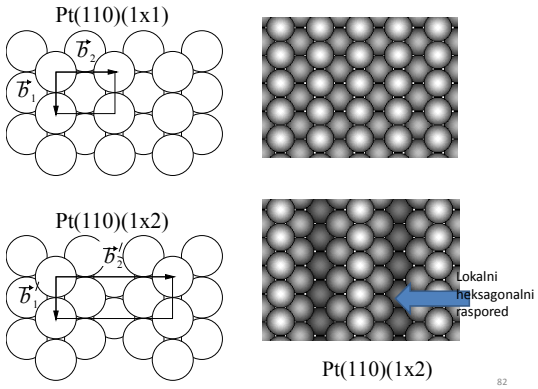
Si(111)-(7x7)



Wood-ova notacija: površinske strukture

fcc (100) face fcc (110) face fcc (111) face





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Adsorpcija

- Šta je pokreće
- Kako izgledaju adsorbovani slojevi
- Adsorpcioni trendovi

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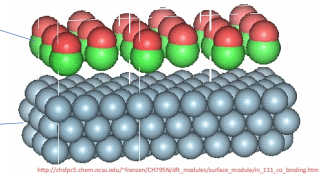
Key Terms

Adsorbat

Adsorbens

Substrat



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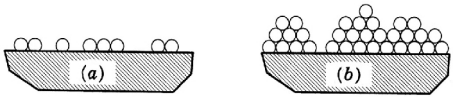
Overview

Fizičke sile - fizisorpcija
- Dipol-dipol
- korelacija

Hemijske sile – hemisorpcija
- preraspodela naelektrisanja

Gustine slične tečnostima

(1 gm/cm^3)=10^{15} molekula/cm^2



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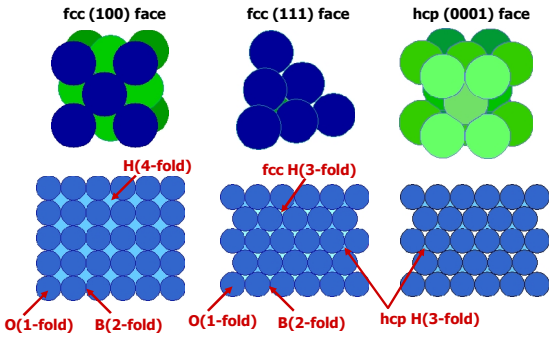
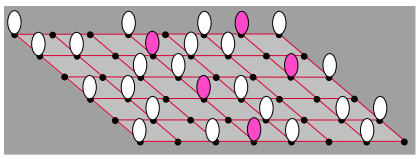
Adsorpciona mesta



Geometrija adsorbovanih slojeva

Struktura adsorbovanih slojeva je uslovljena strukturom substrata



Lengmirovov tip adsorpcije na čvrstoj površini

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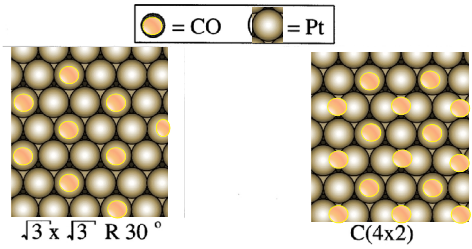
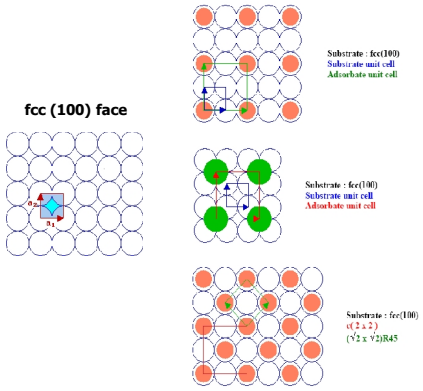
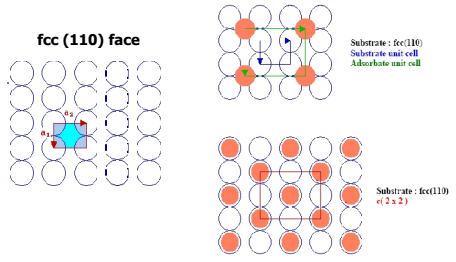
CO na Pt(111)



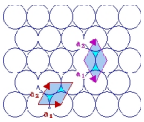
Crossley & King [1980]

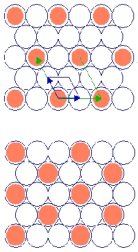
88



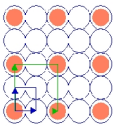


fcc (111) face



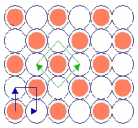


Adsorbovani sloj: matrična notacija



Substrate : fcc (100)
(2 x 2) overlayer

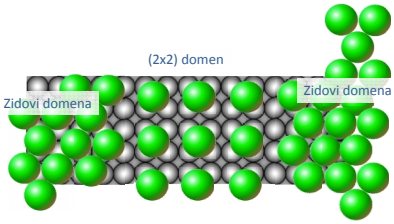
$$b_1 = 2 \cdot a_1 + 0 \cdot a_2 \quad b_2 = 0 \cdot a_1 + 2 \cdot a_2 \quad \Rightarrow \quad M = \begin{bmatrix} 2 & 0 \\ 0 & 2 \end{bmatrix}$$



Substrate : fcc (100)
c(2 x 2) overlayer

$$b_1 = 1 \cdot a_1 + 1 \cdot a_2 \quad b_2 = -1 \cdot a_1 + 1 \cdot a_2 \quad \Rightarrow \quad M = \begin{bmatrix} 1 & 1 \\ -1 & 1 \end{bmatrix}$$

Incommensurate Adsorption



Persson et al. [1990].)

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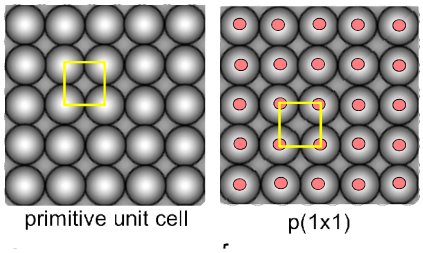
Kvadratna rešetka



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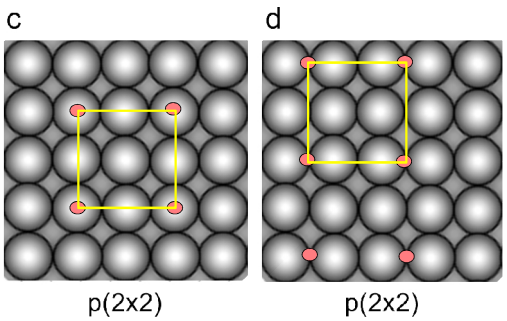
Kvadratna rešetka



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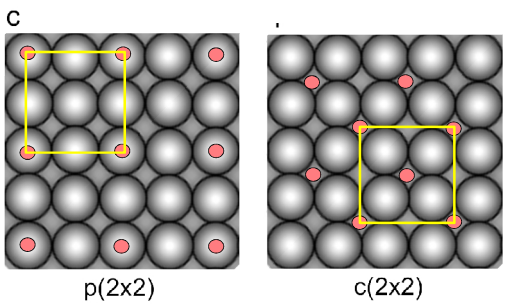
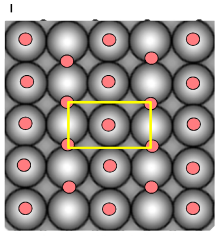
Primitivna i centrirana rešetka

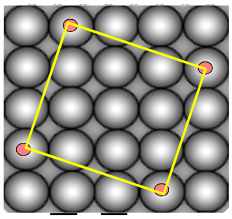


96

Kvadratna rešetka



p(2x1)



$\sqrt{10} \times \sqrt{10}\ R18.4^\circ$

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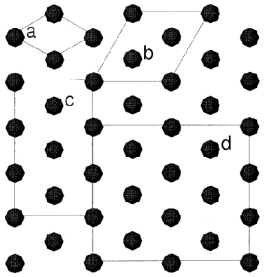
$CH_3S/Au(111)$



Θ	site	Δz	S–M	E_{ads}	cell
1	~on-top	2.84	3.00	4.4	*c*
1	~on-top	2.86	3.00	5.8	*d*
0.5	~on-top	2.84	2.95	5.9	*d*
1	fcc hollow	1.81	2.55	2.9	*b*
0.5	fcc hollow	1.60	2.51	11.5	*c*
0.25	fcc hollow	1.55	2.51	18.3	*d*
1	hcp hollow	1.90	2.60	−1.1	*b*
0.5	hcp hollow	1.70	2.53	4.7	*c*
1	bridge	2.08	2.57	18.6	*b*
0.5	bridge	2.07	2.50	19.6	*c*
0.25	bridge	2.05	2.49	21.8	*d*

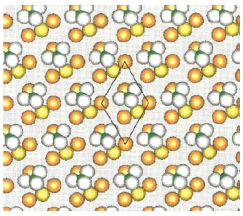
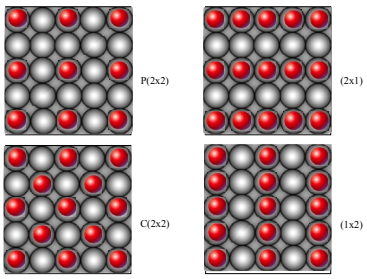


Figure 1. Surface cells used in the calculations. (a) (1 × 1); (b) $(\sqrt{3} \times \sqrt{3})R30$; (c) (3 × $\sqrt{3}$); (d) (3 × 2 $\sqrt{3}$). These cells contain 1, 3, 6, and 12 Au atoms per layer, respectively. Cell d corresponds to the $c(4 \times 2)$ superlattice of the $(\sqrt{3} \times \sqrt{3})R30$ lattice

Adsorpcija CO na kvadratnoj rešetki – adsorbovane faze



The absorption of molecules in a p(2x2), C(2x2), (2x1) overlayer. The dark circles represent sites, the red circles represent adsorption on the sites.

Hemisorpcija na metalima

- Metali imaju mnogo slobodnih elektrona koji učestvuju u vezivanju
- Veza je delokalizovana
- Elektroni su pokretni

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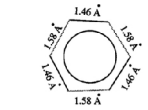
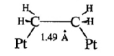
Adsorpcija je kompromis – da bude dobro i adsorbatu i substratu
Mehanizam aktivacije hemijske veze u katalizi

Gaseous Benzene

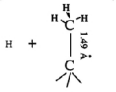


(3x3) Benzene On Rh(111)

Gaseous Ethylene



Ethylene On 100 K Pt(111)



Ethylene On 300 K Pt(111)

Gaseous Hydrogen

Hydrogen On Platinum

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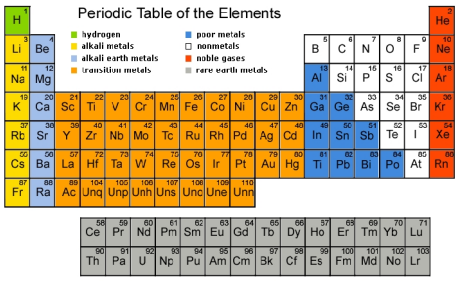
Trendovi u periodnom sistemu



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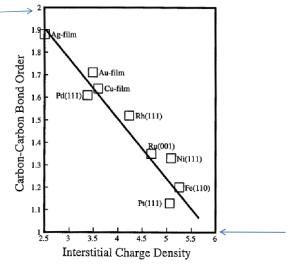
Često dobra korelacija između elektronske gustine, elektronegativnosti i adsorpcionih svojstava

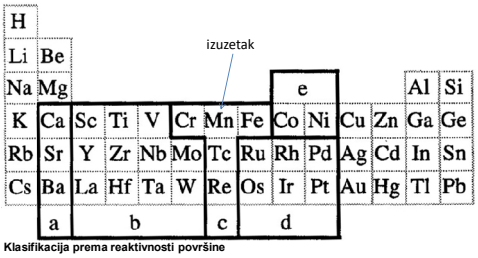
Etilen u gasnoj fazi



Red C-C veze u adsorbovanom etilenu

Sigma veze

Adsorpcija kroz periodni sistem

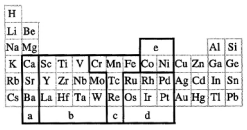


Klasifikacija prema reaktivnosti površine

Slično se ponašaju površine metala koji imaju slične elektronske gustine i elektronegativnosti

Kvalitativni aspekti

			Adsorbing Gas	
Metal	H_2	O_2	N_2	CO
Group a	2 or 3	3	2	3
Group b	3	3	3	3
Group c	3	3	2	3
Group d	3	3	2	3
Group e	3	3	2	3
Cu	2	3	2	1
Ag	0	2 or 3	0	0
Au	0	0	0	3
Al	0	*def*-3	0	3
K, Na, Li	0	3	0	0

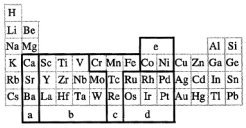


Nedovoljna elektronska gustina

0 – nema adsorpcije
1 – ima na 100 K ali nema na 300 K
2 – aktivirani proces
3 – brza adsorpcija na sobnoj temperaturi

Kvalitativni aspekti

			Adsorbing	Gas
Metal	H_2	O_2	N_2	CO
Si, Ge	0 or 2	3	0	0
InP	0	3	0	0
NiO	0	1		
ZnO	*def*-3	*def*-3	?	1
MgO				
Al_2O_3	0	1		
SiO_2	*def*-2	*def*-3		
NaCl	*0*	*?*	1	0-100K
LiF				1-40 K



0 – nema adsorpcije
1 – ima na 100 K ali nema na 300 K
2 – aktivirani proces
3 – brza adsorpcija na sobnoj temperaturi

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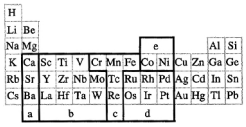
Kvalitativni aspekti

Metal	C_2H_2 C_2H_4	CH_4 C_2H_6	CH_3OH	H_2O
Group a	3	?	?	3
Group b	3	2	3	?
Group c	3	?	3	1
Group d	3	2	3	1
Group e	3	2	3	1
Cu	1 or 3	0	1	1
Ag	1	0	1	1
Au	3	0	1	1
Al	2	?	3	3
K, Na, Li	3 C_2H_2 0 C_2H_4	?	?	3



0 – nema adsorpcije
1 – ima na 100 K ali nema na 300 K
2 – aktivirani proces
3 – brza adsorpcija na sobnoj temperaturi

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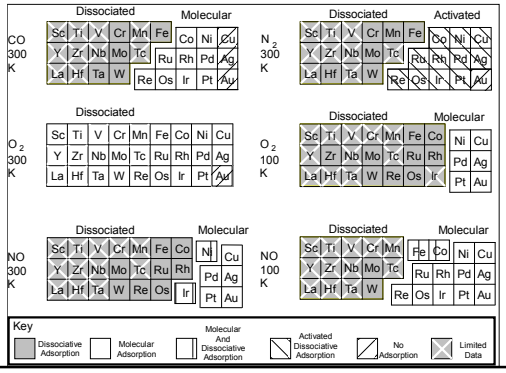
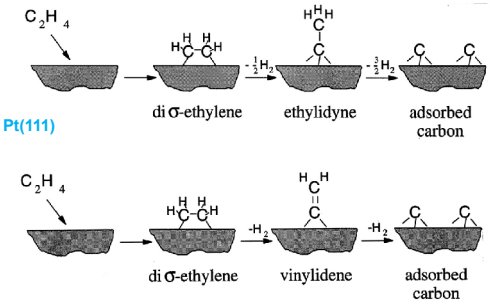
Molekulska i disocijativna adsorpcija

Brodén et al. [1976]

10^{-6} torr



Strukturna osetljivost



Različite klase adsorbata na metalnim površinama

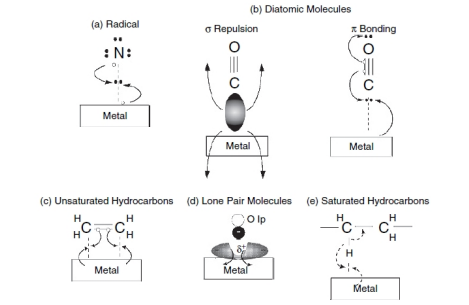
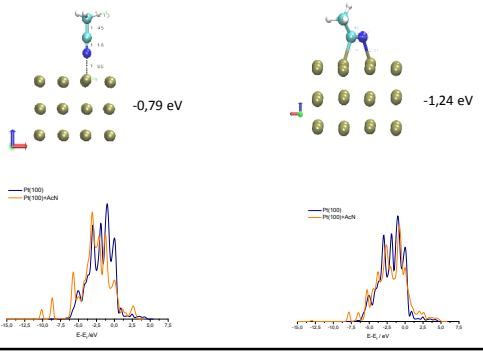


Figure 2.58. Schematic illustrations of the five different types of chemical bond formation on metal surfaces.

Primer: AcN na Pt(001)



Korelacija sa elektronskom strukturom

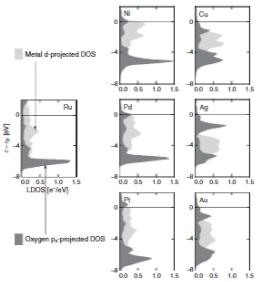


Figure 4.2. The density of states projected onto the d states of the surface atoms for the surfaces considered in Figure 4.1 (grey). Also shown (black) is the oxygen $2p_x$ projected density of states for O adsorbed on the same surfaces. The formation of bonding and anti-bonding states below and above the metal d states is clearly seen. Adapted from Ref. [4].

Korelacija sa elektronskom strukturom

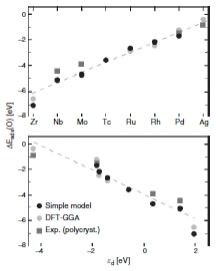
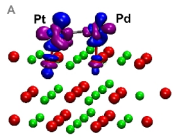


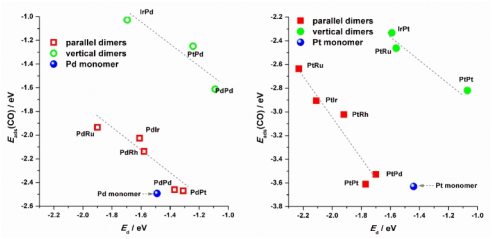
Figure 4.6. Variations in the O adsorption energy along the 4d transition metal series. The results of full DFT calculations are compared to those from the simple d band model and to experiments. Below the same data are plotted as a function of the d band center. Adapted from Ref. [4].

Energije adsorpcije mnogih jednostavnih adsorbata se korelišu sa centrom d-trake metalnog subtrata

Adsorpcija na nisko-koordinisanim metalnim atomima
(defekti, kinkovi, stepenice, adsorbovani klasteri – katalizatori!)

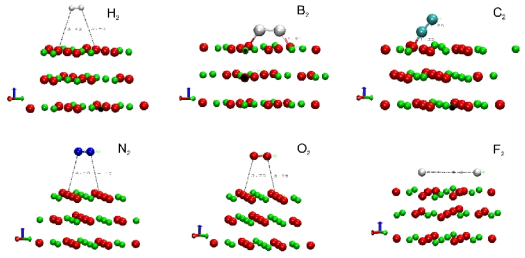


Nema jedinstvene teorije

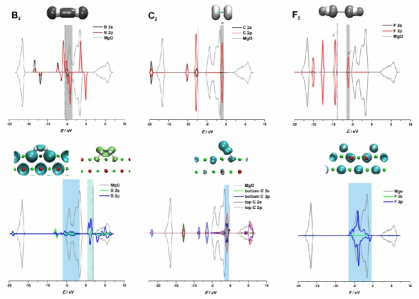


Adsorpcija na oksidima – nema jedinstvene teorije
Primer: X_2@MgO(001)

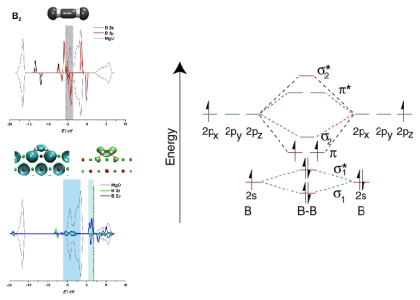
Svojstva jonskih kristala!!!



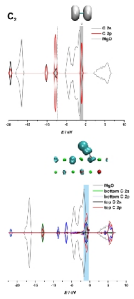
Adsorpcija na oksidima – nema jedinstvene teorije
Primer: C_2@MgO(001)

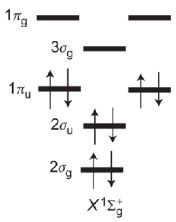


Adsorpcija na oksidima – nema jedinstvene teorije
Primer: B_2@MgO(001)



Adsorpcija na oksidima – nema jedinstvene teorije
Primer: C_2@MgO(001)





Adsorpcija na oksidima – nema jedinstvene teorije
Primer: F_2@MgO(001)