1.9 The work function of Pt(111) is 5.93 eV. A Ru film has a work function of 4.71 eV. If Ru islands are deposited on a Pt(111) surface, in which direction does electron transfer occur?

1.10 Redraw Fig. 1.13 for a p-type semiconductor [65, 67].

1.11 Given that the partition function, q, is defined by a summation over all states according to

$$q = \sum_{i=1}^{\infty} \exp(-E_i/k_B T) \quad (1.8.3)$$

where E_i is the energy of the ith state. Use Eq. (1.4.4) to show that the mean vibrational energy of a solid at equilibrium is given by Eq. (1.4.6). Hint: The mean energy is given by

$$\langle E \rangle = k_B T^2 \frac{\partial(\ln q)}{\partial T} \quad (1.8.4)$$

1.12 The Debye temperature,

$$\theta_D = \hbar\omega_D/k_B, \quad (1.8.5)$$

is more commonly tabulated and determined than is the Debye frequency because of its relationship to the thermodynamic properties of solids.

(a) Calculate the Debye frequencies of the elemental solids listed in Table 1.3 in Hz, meV and cm^{-1}.

(b) Calculate the mean phonon occupation number at the Debye frequency and room temperature for each of these materials at 100, 300 and 1000 K.

1.13 The Debye model (see Table 1.3) can be used to calculate the mean square displacement of an oscillator in a solid. In the high-temperature limit this is given by

$$\langle u^2 \rangle = \frac{3N_A \hbar^2 T}{M k_B \theta_D^2} \quad (1.8.6)$$

Table 1.3 Debye temperatures, θ_D, for selected elements; see Exercises 1.12, 1.13 and 1.14

	Ag	Au	diamond	graphite	Pt	Si	W
θ_D (K)	225	165	2230	760	240	645	400

(a) Compare the root-mean-square displacements of Pt at 300 K to that at its melting point (2045 K). What is the fractional displacement of the metal atoms relative to the interatomic distance at the melting temperature?

(b) Compare this to the root-mean-square displacement of the C atoms at the surface of diamond at the same two temperatures.

1.14 The surface Debye temperature of Pt(100) is 110 K. Take the definition of melting to be the point at which the fractional displacement relative to the lattice constant is equal to ~8.3% (Lindemann criterion [83, 84]). What is the surface melting temperature of Pt(100)? What is the implication of a surface that melts at a lower temperature than the bulk?

1.12 in 2nd edition

1.15 The bulk terminated Si(100)–(1 × 1) surface has two dangling bonds per surface atom and is, therefore, unstable toward reconstruction. Approximate the dangling bonds as effectively being half-filled sp^3 orbitals. The driving force of reconstruction is the removal of dangling bonds.

(a) The stable room temperature surface reconstructs into a (2 × 1) unit cell in which the surface atoms move closer to each other in one direction but the distance is not changed in the perpendicular direction. Discuss how the loss of one … to the formation of a (2 × 1) unit cell. Hint: The neares… dimers.

(b) This leaves one dangling bond per surface atom. Descri… dangling bonds that leads to (i) symmetric dimers and (…

(c) Predict the effect of hydrogen adsorption on the symmetr… Hint: Consider first the types of bonds that sp^3 orbit… dangling bonds represent two degenerate electronic stat…

1.16 Describe the features a, b, c, and d in Fig. 1.21.

1.17 What is the significance of a band gap? What differentiates a…

1.18 What are E_g, E_F, E_C, E_V and E_{vac} as shown, for instance, i…

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elements; see Exercises 1.12, 1.13 and 1.14

nd	graphite	Pt	Si	W
0	760	240	645	400

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perpendicular direction. Discuss how the loss of one dangling bond on each Si atom leads to the formation of a (2 × 1) unit cell. Hint: The nearest neighbour surface Si atoms are called dimers.

(b) This leaves one dangling bond per surface atom. Describe the nature of the interaction of these dangling bonds that leads to (i) symmetric dimers and (ii) tilted dimers.

(c) Predict the effect of hydrogen adsorption on the symmetry of these two types of dimers [51, 52]. Hint: Consider first the types of bonds that sp^3 orbitals can make. Second, two equivalent dangling bonds represent two degenerate electronic states.

1.16 Describe the features a, b, c, and d in Fig. 1.21.

1.17 What is the significance of a band gap? What differentiates a partial band gap from a full band gap?

1.18 What are E_g, E_F, E_C, E_V and E_{vac} as shown, for instance, in Fig. 1.21?

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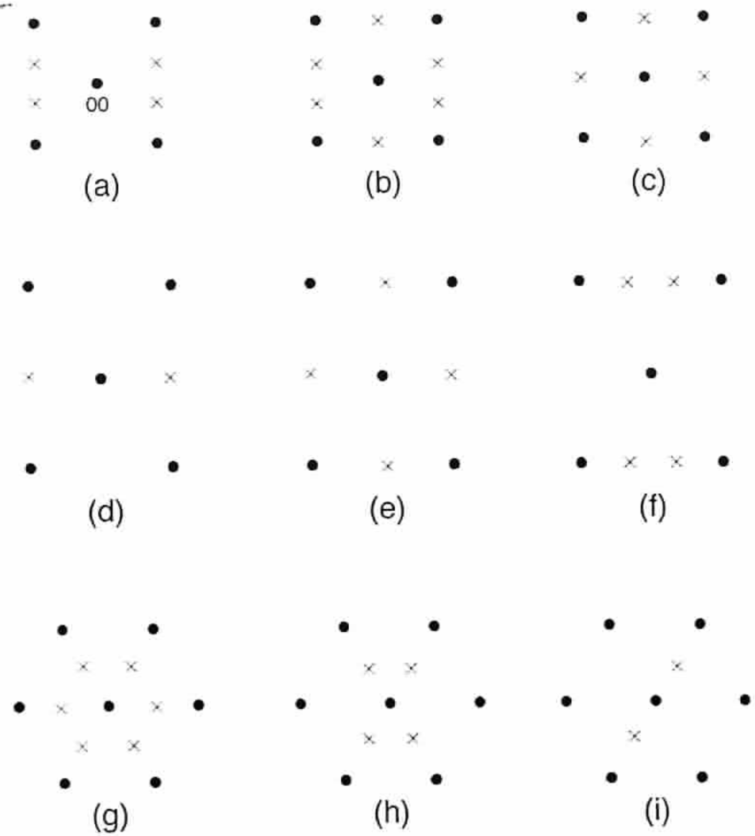

Figure 2.32 *Low-energy electron diffraction (LEED) patterns (a)–(i): see Exercise 2.13.*

2.12 Fractional *coverage* can be defined as the number of adsorbates divided by the number of surface atoms:

$$\theta = \frac{N_{ads}}{N_0}. \qquad (2.12.3)$$

For each of the structures in Exercise 2.11, calculate the coverage. Note any correlations between coverage and the LEED patterns.

2.13 Given LEED patterns (a)–(i) in Figure 2.32 obtained from adsorbate-covered face-centred cubic (fcc) substrates, determine the surface structures. Substrate reflexes are marked • while the additional adsorbate induced reflexes are marked ×. Assume no reconstruction of the surface.

2.14 Determine all of the X-ray levels that all possible for the $n = 3$ shell.

2.15 Explain why Auger electron spectroscopy is surface sensitive. Are Auger peaks recorded at 90, 350 and 1500 eV equally surface sensitive?

2.16 The Auger data for the intensity of the Pt transition at 267 eV and the C transition at 272 eV found in Table 2.3 was taken for adsorption of CH_4 on Pt(111) at

Table 2.3 *Integrated Auger peak areas measured for Pt and C after dosi*

$\varepsilon/10^{20}$ cm^{-2}	I_{Pt}
0	11 350.8
0.1758	10 248.4
1.593	11 693.5
2.477	11 360.1
3.454	10 967.6
4.290	11 610.2
5.071	9626.0
6.188	11 313.7
9.957	11 575.4
14.20	10 964.3
17.35	10 864.1
21.49	11 850.8
25.65	12 912.7
30.51	11 529.1
48.75	10 791.4

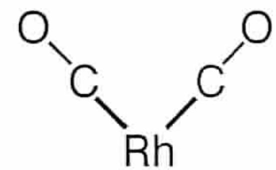

Figure 2.33 *CO adsorbed as a gem-dicarbonyl on rhodium atoms pres substrate (substrate not shown).*

$T_s = 800$ K, $T_{gas} = 298$ K. At this temperature CH_4 dissociates leaving on C(a) on the surface. Use the data to make a plot of θ_{Pt} a exposure, ε, in other words make a plot of the uncovered and cove as a function of ε. The AES sensitivity factors are $s_{Pt} = 0.030$ a

2.17 Consider the spectrum of adsorbed CO in Figure 2.26. CO is ads dicarbonyl on the Rh atoms present on the Al_2O_3 substrate as sho 2.33.

(a) If the CO molecules in the gem-dicarbonyl were independent one CO stretch peak would be observed. Explain why there the spectrum.[107]

(b) Explain why substitution of ^{18}O for ^{16}O changes the positio

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3.5 CO bound to Pt(111) submerged in 0.1 M $HClO_4$ exhibits an FTIR peak associated with a linear bond on-top species at 2070 cm^{-1}.[246] 0.6 ML of Ru is deposited on the Pt(111) electrode to form islands of Ru. When CO is adsorbed on the resulting surface the peak at 2070 cm^{-1} shifts by -10 cm^{-1} and decreases in intensity while a new peak appears at 1999 cm^{-1}. The new peak is shifted by $+6$ cm^{-1} compared with the peak associated with CO bound in an on top site on a clean Ru electrode. Interpret the data as to where and how the CO is bound.

3.6 The amount of energy, δE, transferred in the collision of a molecule with a chain of atoms in the limit of a fast, impulsive collision (that is, a collision that is fast compared with the time that it takes the struck atom to recoil and transfer energy to the chain) is given by the *Baule formula*,

$$\delta E = \frac{4\mu}{(1+\mu)^2}(E_i + q_{ads}). \tag{3.19.3}$$

where $\mu = M/m$, M = the mass of the molecule, m is the mass of one chain atom, E_i is the initial kinetic energy of the molecule before it is accelerated by q_{ads} (the depth of the attractive well, effectively the heat of adsorption). Estimate the energy transfer for H_2, CH_4 and O_2 incident upon copper or platinum chains. Take the incident energy to be
(a) the mean kinetic energy at 300 K;
(b) $E_K = 1.0$ eV.
Take the well depths to be 20 meV, 50 meV and 200 meV for H_2, CH_4 and O_2, respectively.

3.7 When an molecule strikes a surface it loses on average an amount of energy $\langle \Delta E \rangle$ given by[158]

$$\langle \Delta E \rangle = -\gamma \alpha_{disp} E, \tag{3.19.4}$$

where γ is a constant characteristic of the potential energy surface (PES), α_{disp} is a constant that depends on the collision partners and E is the kinetic energy upon collision. For H/Cu(111), $\alpha_{disp} = 0.0024$, $\gamma = 4.0$ and the binding energy chemisorbed H is 2.5 eV.
(a) For an H atom with an initial $E_K = 0.1$ eV 10 Å away from the surface, calculate the energy transfer on the first bounce.
(b) Assuming the same amount of energy transfer on each subsequent collision, how many collisions are required for the H atom to reach the bottom of the well?
(c) Given that α_{disp} changes from one molecule to the next, analogous to the Baule formula we write

$$\alpha_{disp} = k\frac{4\mu}{(1+\mu)^2}, \tag{3.19.5}$$

where μ is calculated assuming one surface atom participates in the collision. Then make calculate α_{disp} for CO assuming the same proportionality factor as for H. Then make a rough estimate of the number of collisions CO with an initial kinetic energy of 0.1 eV requires to reach the bottom of a 1.2 eV chemisorption well assuming

3.8 Classically, a chemical reaction cannot occur if the collisi sufficient energy to overcome the activation barrier. This am of energy are the basis of the Arrhenius formulation of re an atom, the thermal energy is distributed over the translati The velocity distribution is governed by the *Maxwell distr*

$$f(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 \exp\left(\frac{-Mv^2}{2RT}\right).$$

where M is the molar mass and v the speed. Assumin requirement for sticking, i.e., that energy is the only determ sticking coefficient of an atomic gas held at
(a) 300 K and
(b) 1000 K
for adsorption activation barriers of $E_{ads} = 0, 0.1, 0.5$ anc

3.9 A real molecule has quantized rotational and vibration en *Boltzmann distribution* law describes the occupation of the among rotational levels is given by

$$N_{v,J} = N_v \frac{hc}{k_B T}(2J+1)\exp\left(\frac{-E_{rot}}{k_B T}\right).$$

where $N_{v,J}$ is the number of molecules in the rotational st v and J and N_v is the total number of molecules in the vibr of rigid rotor levels is given by

$$E_{rot} = hcB_v J(J+1).$$

where B_v is the rotational constant of the appropri vibrational population is distributed according to

$$N_v = N\exp\left(\frac{-hcG_0(v)}{k_B T}\right),$$

where N is the total number of molecules and $G_0(v)$ vibrational level v above the ground vibrational level. mean energy is distributed according to

$$\langle E \rangle = \langle E_{trans} \rangle + \langle E_{rot} \rangle + \langle E_{vib} \rangle.$$

where for a diatomic molecule

$$\langle E_{trans} \rangle = 2k_B T$$
$$\langle E_{rot} \rangle = k_B T$$
$$\langle E_{vib} \rangle = \sum_{n=0} \frac{h\nu_n}{\exp(h\nu_n/k_B T) - 1}.$$

Note that this neglects the contribution of zero-point energy.

5.12 Exercises

5.1 Derive the Young Equation, Equation (5.3.1)

5.2 Consider a hemispherical liquid island of radius r with surface energies $\gamma_{ls} > \gamma_{lg}$ in equilibrium with its vapour. Calculate the island surface energy as a function of r and demonstrate that small islands are unstable with respect to large islands. Assume the substrate to be rigid and that the island energy is composed only of island–substrate and island–vapour terms.

5.3 Consider the dynamics of deposition of X, Y and Z multilayer films. For each case, determine whether deposition occurs on the downstroke (insertion of substrate into the LB trough), upstroke (retraction) or in both directions. Discuss the reasons for these dependencies.

5.4 The *sticking coefficient* is defined as

$$s = \frac{r_{\text{ads}}}{Z_{\text{w}}} \tag{5.12.1}$$

and represents the probability of a successful adsorption event. The collision frequency in solution is given by

$$Z_{\text{w}} = c_{\text{sol}} \left(\frac{k_{\text{B}}T}{2\pi m} \right)^{1/2} \tag{5.12.2}$$

where c_{sol} is the concentration in molecules per cubic metre. The initial sticking coefficient of $CH_3(CH_2)_7SH$ on a gold film is 9×10^{-8}.[40] Assuming a constant sticking coefficient, which is valid only at low coverage, estimate the time required to achieve a coverage of 0.01 ML for adsorption from a 5×10^{-3} mol l^{-1} solution. Take the surface density of atoms to be $1 \times 10^{19}\,\text{m}^{-2}$.

5.5 Your lab partner has prepared two Si crystals but has not labelled them. One is H-terminated, the other is terminated with an oxide layer. Propose and explain an experiment you could perform in your kitchen that would distinguish the two.

5.6 Explain the observed trend that C_4 straight-chain amphiphile generally do not form LB films or SAMs that exhibit a structure that is as well ordered as that of C_{12} straight-chain amphiphiles.

5.7 Describe what would occur during vertical deposition of a LB film if the barriers of the trough were stationary and a large surface area substrate were used.

5.8 After a 4 h exposure to pure, deoxygenated H_2O, a H-terminated Si(111) surface is found to have an oxygen atom coverage of 0.6 ML measured with respect to the number of Si atoms in the Si(111)–(1×) layer. Estimate the sticking coefficient (i) assuming that all of the oxygen is the result of dissociative H_2O adsorption and (ii) assuming that all of the oxygen results from the adsorption of OH^-.

5.9 Calculate the energy released when H^+(aq) reacts with a dangling bond to form an Si–H bond on an otherwise hydrogen-terminated surface. You will need the following: the ionization potential of H atoms $IP(\text{H}) = 13.61\,\text{eV} = 1313\,\text{kJ mol}^{-1}$; the enthalpy of solvation of protons $\Delta_{\text{solv}}H(\text{H}^+) = -11.92\,\text{eV} = -1150\,\text{kJ mol}^{-1}$ and the Si–H bond strength $D(Si\text{–}H) = 3.05\,\text{eV} = 294\,\text{kJ}$ enthalpy of solvation of the Si dangling bond on an otherwis the same as the enthalpy of solvation of the Si–H unit that i

5.10 When Si is placed in HF(aq) a dark current of about 0.4 μA current is measured in the absence of an applied potentia illumination. Assuming that this dark current is due to an e initiated by the absorption of F^-(aq) and that one electro substrate for every one Si atom that is removed by etching, unilluminated Si in HF(aq).

5.11 Derive the Nernst equation for the Fe^{2+}/Fe^{3+} redox coupl

5.12 The dipole moments of O(a) and OH(a) on Pt(111) ar respectively.[54] Calculate the shift in the adsorption energy c of the electric field in the double layer with the dipoles whe 1 V relative to the point of zero charge.

5.13 Calculate the radius of curvature and discuss capillary co pore that has surfaces with (i) $\psi = 90°$ and (ii) $\psi = 180°$.

5.14 Consider a material with cylindrical pores exposed to air a of 85 %. Into pores of what size will water condense?

5.15 Calculate the effective force due to the capillary force and tl for a porous silicon film with a porosity $\varepsilon = 0.90$ when dri water or ethanol. The mean pore diameter is $r_p = 10$ nm. $\gamma_{\text{water}} = 71.99\,\text{mN m}^{-1}$, $\gamma_{\text{Si}} = 1000\,\text{mN m}^{-1}$, $E_{\text{Si}} = 9.88 \times 1($

5.16 Show that the relative absorption $\Gamma_j^{(1)}$ is independent of th surface.

5.17 Derive Equation (5.7.19).

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nge of final structures ranging from sharp tips to smooth surfaces to porous

n of the surface that is etched can be controlled by the use of a mask.
tive tone resist. the exposed portion of the resist is removed during
ent, whereas in a negative resist the unexposed region is removed.

tiers and Challenges

nctionalization of nanoparticles and the inhibition of nanoparticle aggrega-
of these are essentially growth problems and both have a direct impact on
poration of nanoparticles into nanoparticle/polymer composites. Nanoparti-
er composites can have desirable materials properties. Common examples
Bakelite and tyres but the greatest hurdle to the routine production of
d composites is the lack of cost-effective methods for controlling the
n of nanoparticles within the polymer matrix.[192]
f nanoparticles and nanoparticles aggregates including colloidal crystals and
n of ice particles.
on networks formed during wafer bonding as a method of nanostructure
1.
nents of a theory to describe equilibrium structures in heteroepitaxy.
nent of models to explain the mechanism of catalytic growth and determina-
the limits of catalytic growth to produce nanowires and nanotubes from
materials with controlled sizes and placement.
unified kinetic models can be proposed to explain growth and the dissolution
als[123, 124] in aqueous solutions, how far can a similar unification of underlying
s be achieved to relate growth and etching more generally?
s the first chemical step in the etching of Si in acidic fluoride solution occur?
replace H(a) in a concerted manner or does it abstract H(a) with the resulting
bond capped by F (with injection of an electron into the conduction band) in
d step? Does abstraction play a role in any of the subsequent steps? Is
ion involved in the activation of H-terminated Si surface in its reactions with
molecule such as alkene, alkynes, alcohols, etc.?

rther Reading

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7.13 Exercises

7.1 Dunstan[6] has shown that there is a linear dependence of the $In_xGa_{1-x}As$ lattice constant on the lattice constants of its constituents according to

$$a_{In_xGa_{1-x}As} = x\, a_{InAs} + (1-x)\, a_{GaAs}. \quad (7.16.1)$$

Substitute this dependence into Equation (7.1.3) and derive Equation (7.1.4).

7.2 Consider a system that for a given set of conditions exhibits step-flow growth. Discuss the effects that the adsorption of heteroatoms can have on homoepitaxial growth. Consider two low heteroatom coverage cases: (1) the heteroatoms decorate the steps and (2) the heteroatoms occupied isolated terrace sites.

7.3 Si is the most important semiconductor for electronic applications. GaAs and its III–V sister compounds are better suited than Si as building blocks for optical devices such as light emitting diodes (LEDs) and lasers. The integration of optical components with electronics is a highly desirable manufacturing goal for improved communications, computing and display devices. Discuss fundamental physical reasons why it is difficult to integrate GaAs circuitry with Si.

7.4 Discuss how Auger electron spectroscopy or XPS can be used to distinguish Frank-van der Merwe from Volmer-Weber growth. Hint: Look at Figure 7.3 and consider how the substrate signal varies.

7.5 (a) Consider the epitaxial growth by MBE of $In_{0.67}Al_{0.33}P$ layer on an InGaAs substrate. What must the relative fluxes of In, Al and P be in order to maintain this composition? What influence does the substrate temperature have on epitaxy and the required fluxes?

(b) Consider the CVD growth of P-doped (at a concentration of $10^{16}\ cm^{-3}$) $Si_{(1-x)}Ge_x$ with $x = 0.05$ from the respective hydrides. Discuss the influence of surface temperature on epitaxy and the fluxes required to maintain this composition.

7.6 The dimensionless formation energy $E(V)$ of a single-facetted quantum dot as a function of its dimensionless volume is given by[4]

$$E(V) = \alpha V + \frac{2\beta V^{2/3}}{e^{1/2}} - 2V^{1/3}\ln(e^{1/2}V^{1/3}) \quad (7.16.1)$$

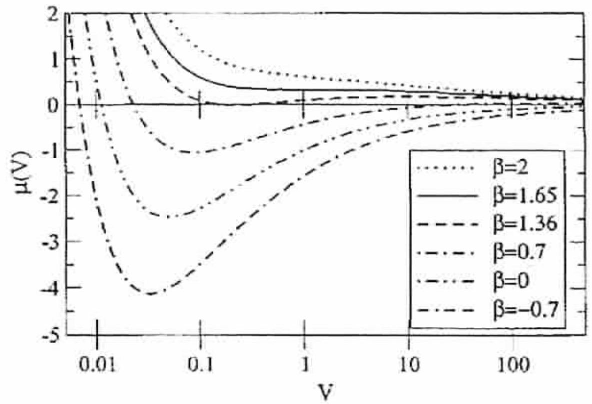

Figure 7.18 Graph of μ vs V. Reproduced from T. P. Munt et al., Appl. Phys. Lett., **85**, 1874. Copyright (2004), with permission from the American Institute of Physics.

Assuming that $\alpha = 0$, predict the most probable island volume for $\beta = 1.4$, 0.5 and −0.5.

7.7 The incident flux can be used to tune the chemical potential of a system of islands on a surface. Predict what occurs to the island size distribution when $\beta = -0.7$ and the flux is turned off for a system with a chemical potential of (a) +1, (b) −3, (c) −4, given the functional form of μ vs V shown in Figure 7.18.

7.8 Design a scheme involving lithography, deposition and etching that will create the structure in Figure 7.19. Hint: The etch rate of SiO_2 is so high compared with that of c-Si that a sacrificial layer of SiO_2 can be removed by HF(aq) without attacking the c-Si.

7.9 Determine the orientation of the pore walls formed on Si(100) given that they are straight and that their orientation with the respect to the {100} planes is as shown in Figure 7.20.

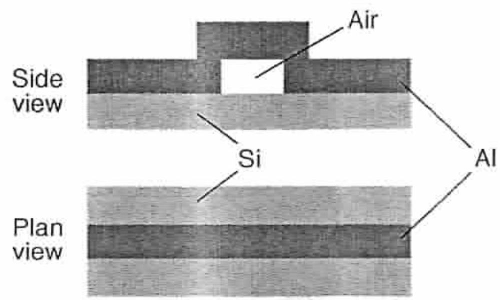

Figure 7.19 Structure to be formed in Example 7.8.

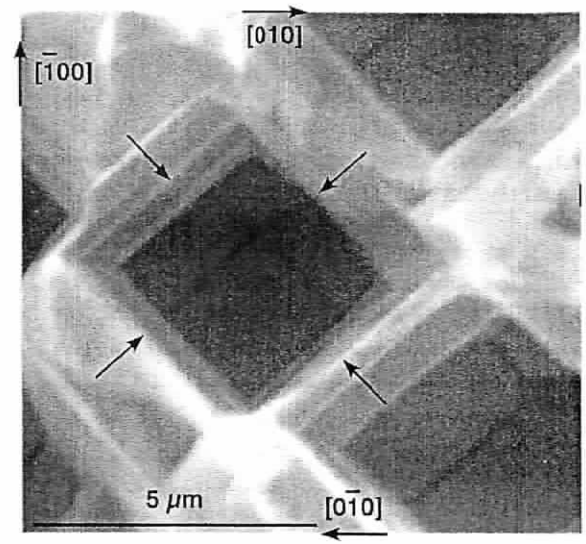

Figure 7.20 Si(100) pore orientation. Reproduced from M. E. Dudle Electrochem. Soc., **155**, H164. Copyright (2008), with permission fro Society.

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