Surface Science

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Examination
June 17, 2015
2-5 pm

Name:………………………………………………………

Student number: ……………………………………………

> This is your original exam. It contains this cover sheet and six questions. Questions #1 and #2 are obligatory. Choose two additional question to answer from the remaining four. Do not hand in the other questions/answers.
>
> Work out more complicated answers on scrap paper before copying the relevant parts onto this original.

Results:

| Question 1	Question 2	Question x	Question x
/25	/25	/25	/25

Total:

Grade:

Question 1   **Surface Crystallography**

Iron is a rather abundant element. The Earth's crust consists for 6.3% of this element. In pure, metallic form, its crystal structure is body centered cubic (BCC) with a lattice constant of 0.287 nm.

a) (5 points) Clearly indicate the positions of the atoms in the cube below for a BCC lattice, indicate the line in the cube in which atoms 'touch' each other, and calculate its length.
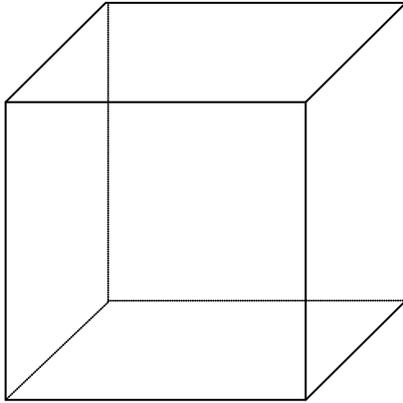
b) (5 points) Make drawings of the surface planes (in the squares below) containing at least 9 atoms each.

(100)	(110)	(111)
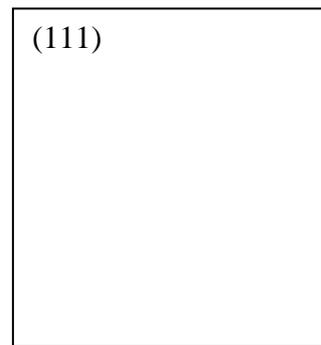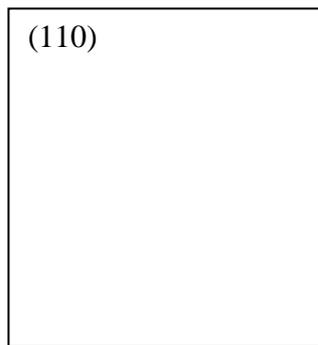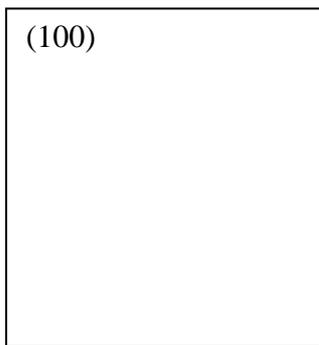
c) (5 points) Discuss the expected order of stability of the Fe(100), Fe(110) and Fe(111) surface planes using surface atom densities.

In one of the last papers studied during the course, DFT calculations were presented on the adsorption and reaction of O_2 and CO adsorption at various forms of the Sn(110) surface. This material has a rutile crystal structure with lattice constants a = 4.737 Å and c = 3.185 Å. The rutile structure is shown below with O in red and Sn in grey.
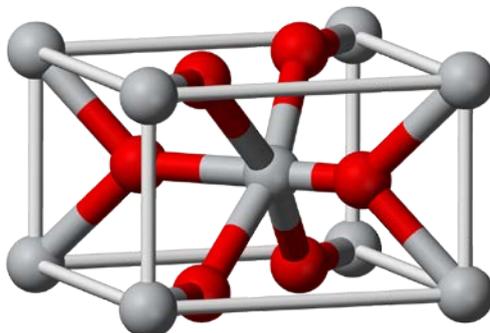
c) (5 points) Indicate and extend the (110) plane in the unit cell above. Subsequently, clearly connect all non-equivalent O and Sn atoms in that plane to their counterparts in the side and top views shown below. Use arrows or labels.
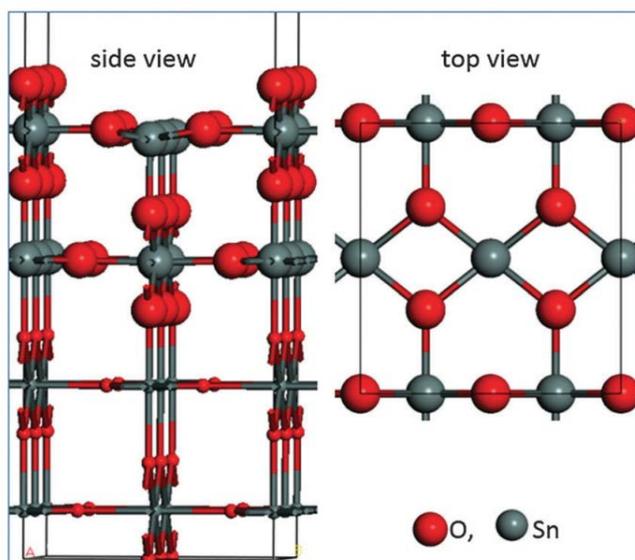

Fig. 1 The SnO$_2$(110) surface.

d) (5 points) In the introduction to the paper, the authors state "However, the SnO_2(001) surface has larger surface energy than that of the (110) surface, which is the most stable low-index SnO_2 surface". Justify this statement.

Question 2   **Diffraction patterns of surfaces and overlayers**

a) (5 points) Describe how the spots in a LEED pattern would evolve if incident molecules adsorbed randomly onto the substrate, forming an ordered overlayer only when the coverage reaches ¼ of a monolayer (with respect to the substrate atoms).

b) (5 points) Prove that the matrix notation for the $\sqrt{3}\times\sqrt{3}$-R30^0 superstructure on the 2D hexagonal lattice is

$$\begin{pmatrix} 2 & 1 \\ -1 & 1 \end{pmatrix}$$

when the basic translation vectors make an angle of 120^0.

c) (5 points) Draw the p(2x2) structure both in real and reciprocal space, using the square paper provided on the next page. Either use calculations involving vectors or chemical intuition, but motivate the way you come to your answer.

d) (5 points) Determine the surface structure from the following LEED pattern from an adsorbate-covered fcc surface. Substrate reflexes are marked by circles, adsorbate reflexes by crosses. Motivate your answer.
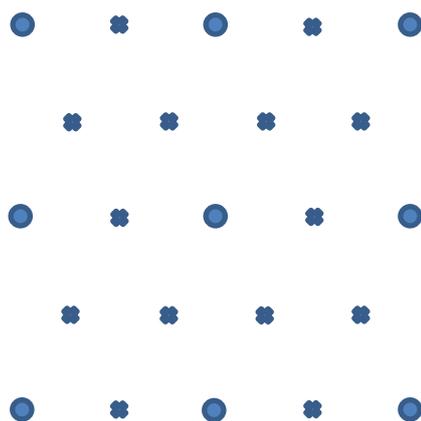
e) (5 points) Using the Ewald construction, evaluate the scale of the recorded diffraction pattern from a surface with a square lattice of period 3 Å. How many diffraction spots are seen in the LEED pattern at energy = 50 eV in a system with a 120^0 hemispherical screen? Use the square paper to make a sketch.

Question 3   Adsorption, diffusion and desorption – van Gastel et al, PRL 2001

Adsorption and desorption are processes that are governed by the potential energy surface describing the interaction of an atom or molecule with a surface.

a) (4 points) Draw a generic 1-dimensional potential energy curve for a molecule, e.g. O_2, that may dissociate on a surface. Assume that dissociation is highly activated. Label all possibly relevant wells in the potential (e.g. $O_{2\,(phys)}$ or $O_{(chem)}$).

b) (6 points) What are the three assumptions of the Langmuir adsorption model and derive the relation between coverage (θ) and pressure (p) for a non-dissociative Langmuir isotherm for the adsorption and desorption rates.

c) (5 points) Consider an fcc (100) surface with a lattice constant of 0.2 nm and an ad-atom hopping in between four-fold hollow sites. Draw using a single x-axis, which represents real space, a generic 1-dimensional potential energy curves for diffusion along the [011] and [010] directions. Clearly indicate which potential belongs to which direction. Briefly state why the diffusion barrier along one direction is likely higher than along the other.
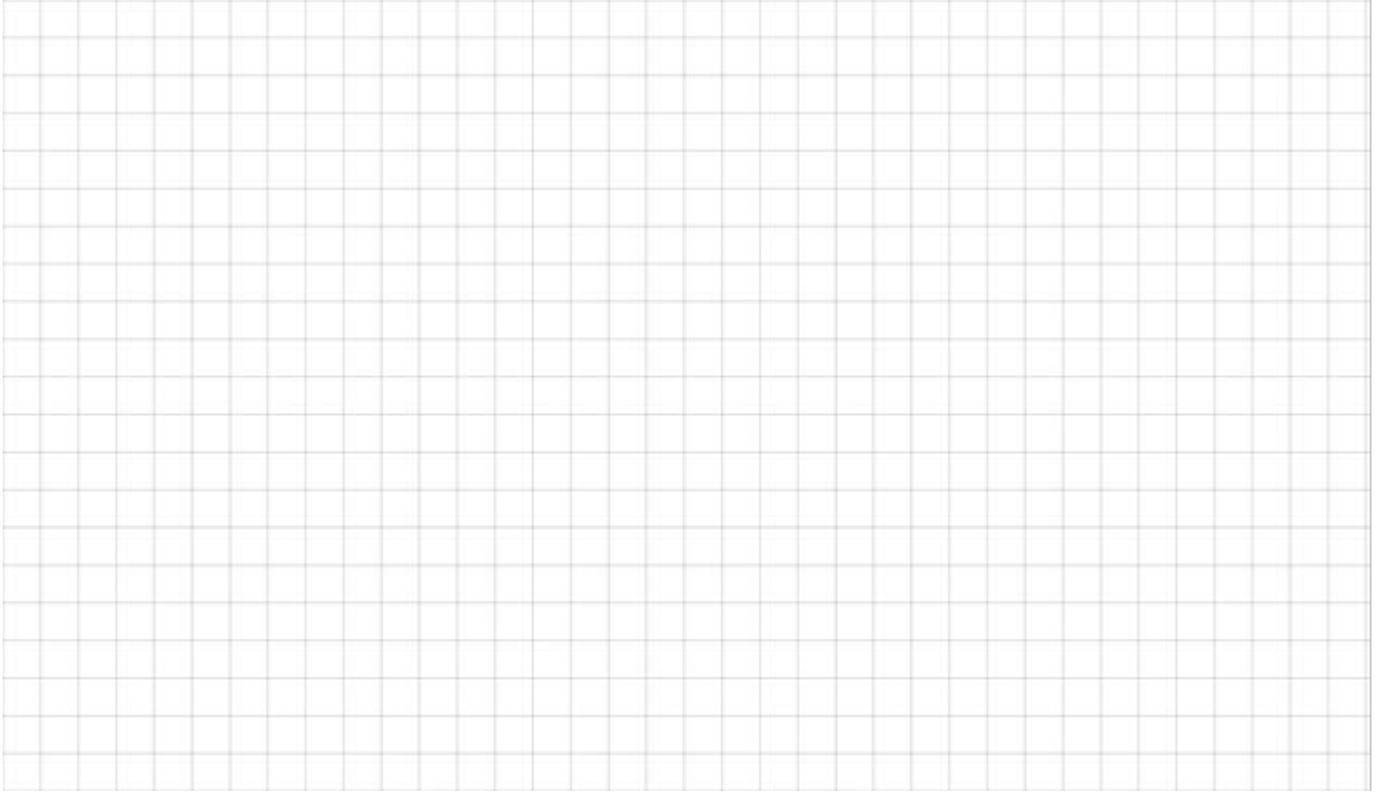
Consider the paper by van Gastel et al. (PRL 2001)

d) (4 points) Using your own words, describe the performed experiment and the reason why it is concluded that the motion of indium atoms result from encounters with a vacancy in the Cu surface.

e) (6 points) In the subsequent article *Surface Science* **521,** 10 (2002), van Gastel et al. provide a schematic of the potential energy diagram for the same system. Explain the diagram and identify all symbols. Then explain why this potential diagram agrees with the findings in the paper published in PRL. Include mentioned values for the formation energy of the vacancy, the diffusion barriers for the vacancy by trading places with In and Cu atoms, and the relative ratio of 10^6 mentioned on page 1654 at the top of the right column in your explanation.
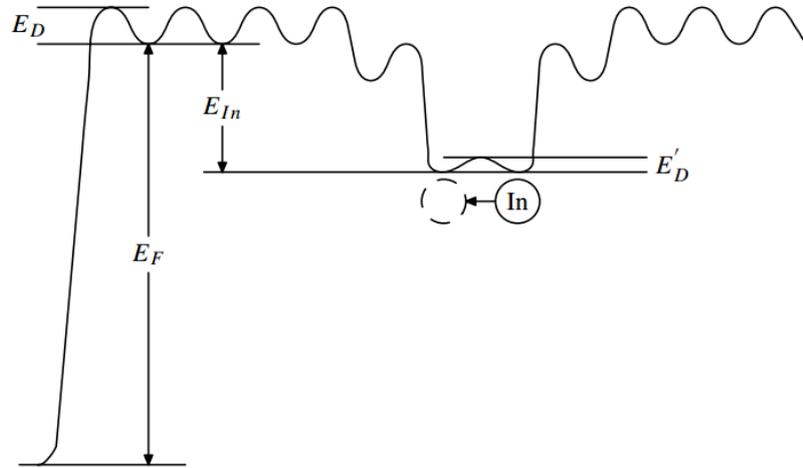
Question 4   **Scanning Tunneling Microscopy – Binnig, PRL 1983**

a) (7 points) Explain the physical principles behind STM using a schematic drawing of the energy levels of the tip and sample involved.

b) (8 points) Describe the two different scanning modes used mainly in STM (i.e. not the spectroscopy mode) and comment which method you would use for which type of experiment.

c) (2 points) In this paper of 1983 by Binnig et al. the authors contribute to the long-standing debate on the surface structure of the Si(111)-7x7 reconstruction. The 7x7 reconstruction is a very complicated surface, and it took the surface science community more than 25 years to fully solve its structure. The combination of different techniques, such as low-energy electron diffraction, scanning tunneling microscopy, and transmission electron diffraction, was used to come to the so-called *DAS-model* for Si(111)-7x7: the *dimer-adatom-stacking fault-model*.

The DAS-model consists of the following elements:

1. The 7x7 unit cell consists of two triangular halves, one of which has a **stacking fault**
2. Nine **dimers** per unit cell bordering the triangular halves of the unit cell
3. Twelve **adatoms** having dangling bonds (a dangling bond is an atom which possesses too few bonding partners to satisfy its valence, and therefore possesses unpaired electrons. For Si they are formed when the Si atom bonds to less than four other Si atoms.)
4. At the corners of the unit cell a twelve-membered ring surrounds a **corner hole**
5. The remaining six atoms, which conserve their dangling bonds, are called **restatoms**

What is the driving force for the observed Si(111) surface reconstruction?

d) (2 points) How many dangling bonds does the reconstructed 7x7 surface have? And how does this amount compare to the amount of dangling bonds in a 7x7 unit cell having an ideal bulk-like termination?

e) (6 points) In the below schematic diagram of the DAS-model (top: top view; bottom: side view) identify the following elements: the two triangular subunits of the 7x7 unit cell, the stacking fault, the dimers, the adatoms, the corner holes, and the restatoms.

$[10\bar{1}]$

$[1\bar{2}1]$
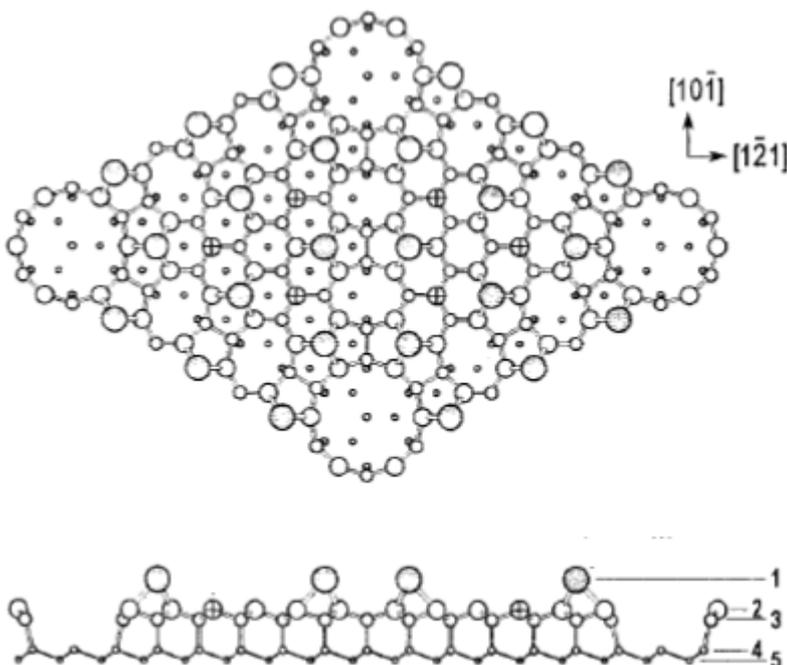
Question 5   **Density Functional Theory – Meyer 2014**

Modeling energy dissipation during chemical reactions at surfaces from *first principles* is still an ongoing challenge. The 'QM/Me' embedding scheme presented in this article provides one step into that direction.

a) (6 points) The authors report a chemisorption energy E_{chem} ~ 2.6 eV for the (dissociative) adsorption of oxygen on the Pd(100) surface. Write down the corresponding energy balance equation according to which E_{chem} is calculated. How many separate density function theory (DFT) calculations are required?

b) (6 points) What is the fundamental theorem of DFT? Which essential approximation to this theorem have the authors made in their study? Give an order magnitude for the error (in eV) this approximation introduces for the calculated adsorption energies.

c) (6 points) The authors do not consider (potential) electron-hole pair excitations in the surface. Which fundamental approximation to the electronic structure problem is this due to? What kind of surface excitations do they include in their model? Which surface reaction mechanism do they predict to occur for O_2 dissociation on Pd(100)?

d) (6 points) In the lecture, two different approaches have been presented for modeling (the geometry) of surfaces in (e.g. DFT) computer codes. Describe both of them including schematic drawings. Which of them is used in the present work? How does it affect modeling energy dissipation?

e) (1 point) Name one DFT code that has been used in any of the papers you have read during the course.

Question 6   **Heterogeneous Catalysis – Honkala et al. Science (2005)**

Particularly in the past, but even today, surface scientists claim that studies using single crystal surfaces performed under UHV conditions are relevant to understanding heterogeneous catalysis. Others point toward significant differences that may be cause for concern.

a) (4 points) Describe in your own words what is meant by the 'pressure gap'.

b) (4 points) Describe in your own words what is meant by the 'materials gap'.

c) (12 points) Summarize *in your own words* the article by Honkala et al (Science, 2005) on the ammonia synthesis. Point out critical assumptions and indicate the strengths of this article.

e) (5 points) Formulate your point of view on the relevance of this study of ammonia synthesis over a ruthenium catalyst. To what extent do you believe it provides a correct picture of the process at the molecular level?