



David Krix, Ulrich Hagemann, Kornelia Huba, and Hermann Nienhaus

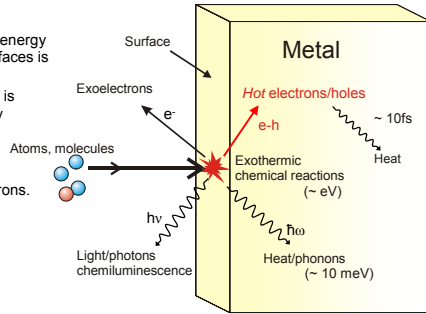
Fachbereich Physik, Universität Duisburg-Essen and CeNIDE

Motivation

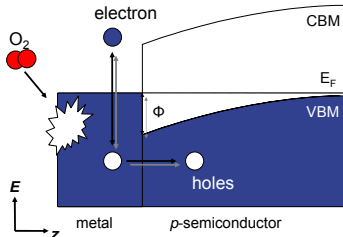
The **fundamental question** is how chemical energy released in exothermic reactions at metal surfaces is dissipated.

Traditionally assumptions are that the energy is **adiabatically dissipated**, i.e. that it is directly converted into heat.

Still there is evidence for significant **non-adiabatic** contributions from electronic excitations, e.g. e-h pairs, photons, exo-electrons.

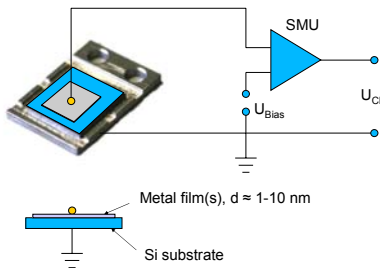


Method



Metal-semiconductor contacts/**Schottky diodes** are used as thin film electronic devices to detect hot charge carriers. Exposing the thin metal film to reactive gases leads to an internal electric current under zero bias conditions. The current is called **chemicurrent** or internal exo-emission current. The current is due to the creation of electron-hole pairs by the chemical reaction.

Experimental setup



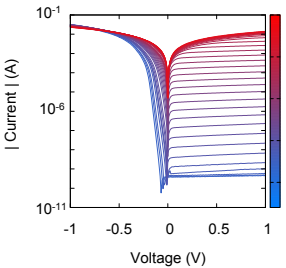
After wet chemical etching (HF) the silicon wafers are mounted to Nb sample carriers and transferred into vacuum.

Pd and alkali films are grown under UHV conditions. During the deposition and later during the measurements the samples can be held in a temperature range between 100 – 600 K.

Samples are contacted by placing a small gold ball onto the metal electrode of the Schottky contact. The highly doped backside of the silicon wafers is used as a low resistance ohmic counter electrode.

Chemically induced currents through the diode down to and below 1 pA can be detected by a source measure unit.

Sample characterisation



The Schottky diodes are characterized electrically by determining the Schottky barrier Φ . A modified version of the Shockley formula

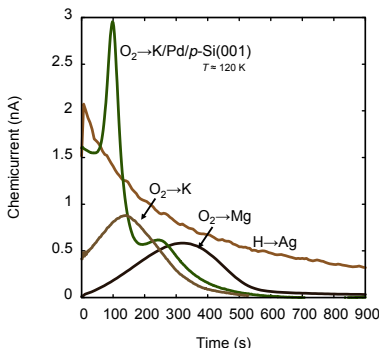
$$I(U, T) = A^{-1} T^2 \exp\left(-\frac{\Phi_{\text{eff}}}{kT}\right) \left(\exp\left(\frac{U - IR}{nkT}\right) - 1\right)$$

describes the I/V-characteristics of inhomogeneous metal-semiconductor contacts.

Pd/p-Si(001) show excellent agreement with the theoretical prediction with temperature independent barrier heights and ideality factor n near one.

$$\Phi_{\text{Pd,p}} \approx 0.4 \text{ eV}$$

Chemicurrents and the role of the reaction kinetics



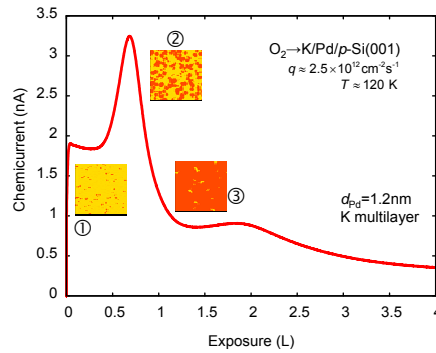
The time evolution of chemicurrents reflects the reactions kinetics. They may be written as the sum

$$j_{\text{ch}}(t) = \sum_i \alpha_i(t) R_i(t)$$

of all process rates involved in the reaction multiplied by a chemicurrent efficiency α .

While atomic hydrogen and oxygen often show a Langmuirian type of kinetics, reactions of O_2 on metallic surfaces are often of nucleation and growth type. That includes that the probability rate is much higher at island edges than on the bare surface.

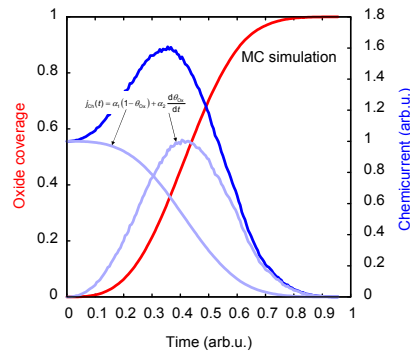
Monte Carlo simulations of experimental data



Chemicurrent vs. time as measured for the oxidation of a potassium multilayer deposited on top of a Pd/p-Si(001)-Schottky diode.

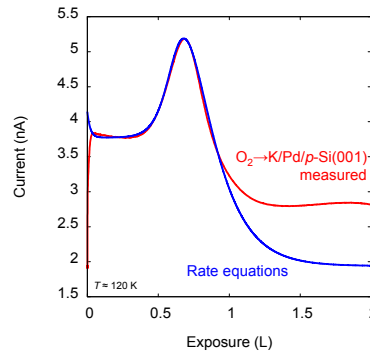
Simulations take into account the existence of a physisorbed oxygen precursor diffusing on the bare metal. The probability of conversion to an oxide state is chosen to be much higher at island boundaries.

Molecular oxygen is allowed to be chemisorbed on the surface in a state different from the oxide.



- Chemisorption of oxygen. Nucleation of oxide islands. $j_1(t) = \alpha_1(1 - \theta_{\text{ox}})$
 - K_2O island nucleation and growth. Maximum in the reaction rate. $j_2(t) = \alpha_2 \frac{d\theta_{\text{ox}}}{dt}$
 - K_2O island coalescence leads to a reduced reaction rate.
- The K_2O islands are further transformed to more oxygen rich species, e.g. K_2O_2 .

Rate equations



An easy set of rate equations may well describe the observed chemicurrents. The equations may be easily modified to also include the second peak.

$$\frac{d\theta_p}{dt} = k_1(1 - \theta_p - \theta_c - \theta_{\text{ox}}) - k_2\theta_p - k_3\theta_p\theta_{\text{ox}}$$

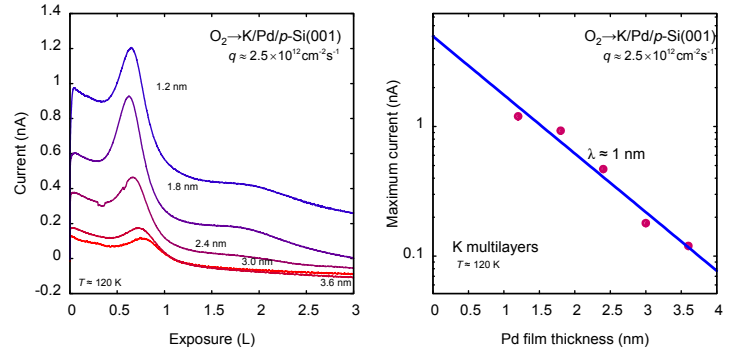
$$\frac{d\theta_c}{dt} = k_4(1 - \theta_p - \theta_c - \theta_{\text{ox}}) - k_5\theta_c$$

$$\frac{d\theta_{\text{ox}}}{dt} = k_6\theta_p\theta_{\text{ox}}$$

$$\Rightarrow j_{\text{ch}} = \alpha_1 k_1 (1 - \theta_p - \theta_c - \theta_{\text{ox}}) + \alpha_2 k_6 \theta_p \theta_{\text{ox}}$$

physisorbed oxygen coverage
chemisorbed oxygen coverage
oxide state (K_2O)

Attenuation by increasing the Pd metal thickness



Ballistic charge carriers as produced during the reaction events are expected to have a very short life time in the metal films. The chemicurrents are thus expected to be attenuated on length scales $1/e$ comparable to the film thickness.

References:

- D. Krix, R. Nünthel, and H. Nienhaus, Phys. Rev. B 75 (2007) 073410.
- S. Glass and H. Nienhaus, Phys. Rev. Lett. 93 (2004) 168302.
- Hermann Nienhaus, Surf. Sci. Rep. 45 (2002) 3.